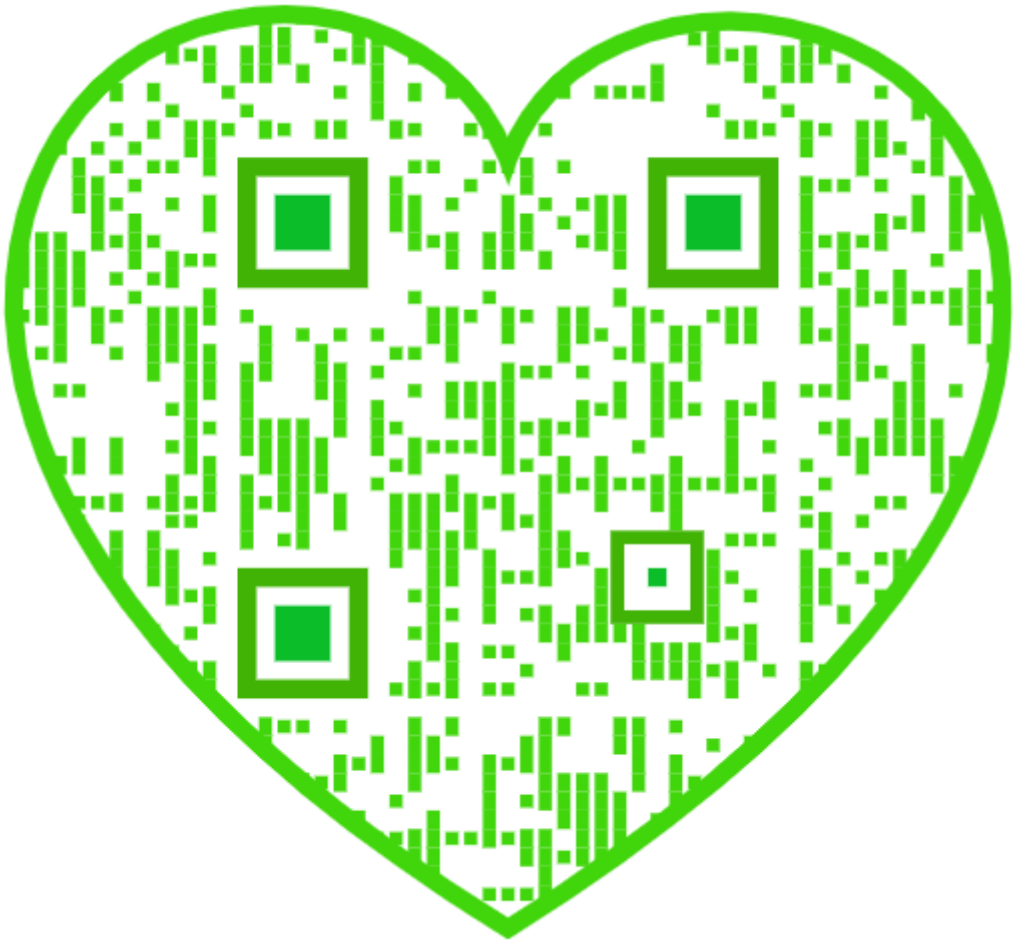

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INDUSTRIAL COLD ADHESIVES

A PRACTICAL HANDBOOK FOR THE MAKER AND USER

BY

ROGER DULAC

ENGLISH EDITION

BY

JOSEPH L. ROSENBAUM

M.Sc., M.I.Chem.E.

LONDON :

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AUTHOR'S PREFACE.

THE published literature on the systematic manufacture of industrial cold adhesives is both scanty and inadequate, despite the steadily and continuously growing importance of the subject as a whole. Recent years, it is true, have seen more interest being taken in the mechanism of adhesive action and in the standardisation of methods of testing, whilst the patent literature, largely owing to the promise of the synthetic resins in the adhesives' field, is growing more voluminous. None the less, so far as the production of the established types of cold adhesives is concerned, the industry is one in which the régime of the "closed door" and the secret process is still very largely in evidence. In the few books on the subject the usual method of treatment is to give a heterogeneous collection of recipes, formulæ and "dodges," selected at random and presented with equal lack of system. Many of these formulæ, which on superficial inspection seem to bear the stamp of practicability, fail when the attempt is made to utilise them in the production of satisfactory commercial products.

The present work has been written "by an industrialist for other industrialists," the subject being considered from its main aspects of raw materials, plant, labour and costs. No complicated formulæ or equations will be found in this book, it having been the author's endeavour to adopt as simple and clear a method of presentation as possible. Only passing reference is made to the ordinary hot glues, the manufacture and use of which are well enough known, whilst there is ample evidence that they are losing ground in the competition with the cold adhesives. This trend is perfectly intelligible. From the viewpoint of the manufacturer, the production of the cold

adhesives is much simpler. No extensive or expensive plant is required, whilst the raw materials for the cold glues are usually both plentiful and cheap. From the viewpoint of the user, the cold adhesives are the more economic products, whilst they are certainly much more convenient to apply. With the continued improvement in the production of cold adhesives, their advantages in the above respects can only, in the writer's opinion, become further accentuated.

The chapter on Plant will be of interest only when the manufacture of cold adhesives is contemplated on a considerable scale. For comparatively small-scale production, either for sale or, more usually, for the makers' own use, there is no need at all for special plant, since in most instances the process is merely a simple cooking operation.

There is one particular aspect of the present work upon which the writer wishes to lay emphasis. The reader will not, except in some exceptional instances, find the formulæ carrying labels, " glue for this " or " glue for that." The reason is very simple. Such indications usually mean very little, since most types of adhesives are capable of finding a fairly extensive field of utilisation. By designating an adhesive made according to a certain formula with a specific label, the reader's attention is unduly attracted to the particular use given, with the result that he is less likely to look around and see whether an alternative type of adhesive may not after all better meet his need. A specific instance will perhaps make our meaning clear. The casein glues are usually grouped under the heading " wood glues," since it is in connection with wood that they find, of course, their main application. But casein glues find numerous other uses, whilst even on wood they may often be advantageously replaced by special starch-base products.

Commercial experience has shown the writer that the question of adhesives is a very complex one indeed, and that the manufacturer is almost daily set new problems by the various users of his materials. To examine every one of these

problems separately would require a book far exceeding the present volume in size, whilst even so, its treatment of its subject would be incomplete and unsystematic. The writer has thought it far preferable to consider the whole subject from the general aspect; to give, so to speak, a general synthesis of the subject and to allow the reader to apply the principles brought out to the special cases he may meet. In short, the author's object has been to produce a work practical before anything else and to guide the reader by indicating to him "why this and not that," "why this combination and not another," what takes place in the various solutions and the directions in which the formulæ can be modified to meet specific cases. Whether he has succeeded is a matter for decision by readers of the volume. To prospective critics, he can only plead in the words of the placard occasionally seen in the epoch of the films of the Far West:—"Don't shoot the pianist, he is doing his best."

The author recognises that owing to the limitations on his time, the work is not complete. He hopes to revise it at a later date and thanks in advance readers who may care to offer him observations and suggestions. Certain of the chapters, it will be noted, contain methods that have not hitherto been published, but which have been applied successfully in industry. Brief references are also made in the text to some of the laboratory investigations that the author has been able to pursue in the limited amount of time which his commercial activities have left him. It is hoped at a later date to complete and publish these investigations, which may be useful to other workers both by suggesting new directions for investigation and by preventing the loss of time which often occurs in carrying out trials that have already been conducted by other workers. The literature on adhesives being, we repeat, very poor, we add our little stone to the edifice in the hope that others will imitate us in the general interest.

ROGER DULAC.

TRANSLATOR'S PREFACE.

THE present English Edition of Roger Dulac's "*Colles à Froid Industrielles*" differs from the French original mainly by the additional chapter on Sodium Silicate Adhesives by Dr. W. S. Macfarlane of Imperial Chemical Industries, Ltd. Sodium silicate in its various grades is a product which already has a very wide utilisation in the field of cold adhesives, mainly, though far from exclusively, in connection with paper and cardboard products, but, as in the case of the starch-derived adhesives, the technical literature on the subject has not hitherto been unduly voluminous.

The information given by M. Dulac on the use of synthetic resins in the adhesives industry has been supplemented in several respects, but no attempt is made to deal with this aspect of the subject in anything approaching completeness. There is no doubt that the future will see a steadily increasing application of products of the synthetic resin type in special problems of industrial adhesion, although they are not likely, on price grounds alone, to compete in the fields now dominated by the starch and dextrin products. As, however, the whole subject of the synthetic resin adhesives is in its infancy, and the published information on the matter still largely confined to patent specifications, it has been thought advisable to defer their systematic treatment until a future edition of "Industrial Cold Adhesives" is called for.

One further point that should be mentioned is that all the processes of adhesives production described in the present work as "Roger Dulac Processes" have been worked out by M. Dulac. Some of them have been, and are being, employed in the industry as secret processes; others have been patented. None of them, however, is at present covered by patent protection and all consequently may be employed by any maker of adhesives.

JOSEPH L. ROSENBAUM.

MANCHESTER, *February*, 1937.

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INDUSTRIAL COLD ADHESIVES.

CHAPTER I.

INTRODUCTORY.

THERE is not, and is not likely to be, an adhesive of universal applicability, for the requirements of the industries using adhesives vary very greatly. Materials of the most divergent types have to be considered in a work portending to cover the adhesives field. In some cases application by mechanical means is essential, in others application by hand brushing is necessary. The effect of slight changes in acidity or alkalinity on the materials being handled, the time which can be allowed for the formation of a strong dried joint and the cost of the adhesive solution are all factors which differ in varying degree from one case to another. For each case, however, there is a particular type of adhesive which most nearly meets requirements. The conditions which a cold glue is required to meet are the following :—

(1) **Mechanical Strength.**—In all cases, even if the material presents certain difficulties in the application of the adhesive, the adhesion must be as perfect as possible, and the strength of the joint when subjected to stress in a direction at right angles to the joint should be, in principle, as great as that of the material itself. The selection and composition of the adhesive are thus mainly dictated by the nature of the material on which it is to be used. The surface of the material is a matter of particular importance, for it will be realised that its smoothness or porosity and its greater or smaller affinity for aqueous solutions have a deciding influence on the type of adhesive that can be used.

When joints of especially high strength are to be made, the adhesion of the glue can be improved by two methods. Firstly, by allowing the coating of adhesive on the two surfaces to thicken before the joint is made by tightening; secondly, and a better method,

the two surfaces are first coated with a dilute solution of the adhesive, which serves as an impregnating agent and fills up any micro-pores in the surface. After this initial coating has thoroughly dried, a second coating of adhesive solution of normal consistency is applied, and when this has been allowed to thicken further, the joint is made. By the employment of such a double system of application the fullest advantage is taken of the intrinsic strength of the adhesive used.

(2) **Resistance to "Degluing."**—It is often highly desirable, and in some cases essential, that the joint made shall be unaffected by continued exposure to humid conditions or even by direct contact with water. Two methods are available for the production of such water-resistant joints: (*a*) By the use of an adhesive originally applied in solution in water but which subsequently becomes insoluble. A drawback to this type of adhesive is that the solutions must be used within a comparatively short time after preparation. Examples of this type of product are to be met with in the cases of formolised gelatin-glue adhesives, lime-caseinate adhesives, etc. (*b*) By the use of an adhesive base which is soluble in a volatile organic solvent, but not in water; latex and cellulose ester adhesives are instances of this type of product.

(3) **Economy or Rapidity.**—According to the class of work to be carried out, the demand will be for a comparatively cheap adhesive or for one which sets rapidly. The latter inevitably are more costly than the slower-setting materials, and it is usually difficult to reconcile the two classes of demand. In the first case solutions or pastes which contain a relatively high percentage of water can be used. On the average, such solutions will contain water to the extent of ten to twelve times the weight of the dry constituents, and are usually further diluted before application. This high ratio of water is made possible by the employment of adhesive bases which themselves possess high swelling power. This viscosity of the original solutions can be increased by chemical reaction upon the adhesive base, or by the addition of cheap secondary materials which function simply as thickening agents. In the second case, rapidity of drying is obtained by (*a*) the utilisation of very concentrated adhesives, that is, products in which the ratio of water to dry material is from 0·40 : 1 to 1·5 : 1; (*b*) the utilisation of solutions of adhesive bases in organic solvents which evaporate very rapidly.

In both these cases the speed of drying can be very markedly influenced with the water-soluble adhesives by the presence of hygroscopic materials, that is, materials which possess a strong affinity for the water in the surrounding atmosphere. Such hygroscopic substances may be added to the rapid-drying aqueous adhesive solution

in small quantities with the object of improving the keeping qualities of such solution. With those rapid-drying adhesives which are solutions in volatile solvents, retardation of the speed of drying is effected by the incorporation of the so-called " plasticisers." These latter are also added with the object of conferring specific properties upon the dried film, as will be shown later.

The thickness and porosity of the materials to be joined also have an influence upon the speed of drying of the adhesive used. When working with impermeable or metallic surfaces, the layer of adhesive in the joint being made is very largely sealed, and drying by evaporation of the water or other solvent can take place only at the edges of the joint, and this is a rather lengthy process. A way out of the difficulty in such cases may be found by the adoption of the dry gluing method mentioned later.

Distinction should always be made, when considering adhesives, between " rapidity of drying " and " speed of setting." In practice the latter is the really interesting factor, as it is the measure of the time necessary before the article being made can be left to itself without any support for the joint. The time which elapses between the joint being made and the article being utilised is in most cases quite ample to permit complete drying and solidification of the film.

Setting in the case of cold adhesives is an accentuation of the more or less sticky initial character of the film, due to evaporation of the solvent.

With ordinary hot glue the set is the solidification by cooling of the layer applied in the hot state.

(4) **Means of Utilisation.**—Adhesives are normally applied by one of the seven following methods, and the method of application should always be taken into account before deciding upon the type of adhesive to be used.

(*a*) *Direct Application by Brushing.*—Further details of this method seem unnecessary. The solution is simply spread directly on the surface to be treated.

(*b*) *Application by the Glazing Method.*—This method is mainly utilised for the application of adhesives to large surfaces of paper and other materials. It is extremely simple and, comparatively, very cheap. The adhesive solution is spread on a zinc sheet and the layer of paper, or other material to be treated, placed on top. Time is allowed for the paste to acquire a suitably sticky consistence before the paper, or other material, is removed with the paste adhering to it.

(*c*) *Application by the Dry Method.*—The process is as follows:—The surfaces to be joined are coated with adhesive solution, this

solution being allowed to dry completely. The joint is then made by bringing the two surfaces into juxtaposition and subjecting them to the influence of a heated press. The adhesive layers are softened momentarily and the joint is satisfactorily made. The interest of this process is that it allows of instantaneous gluing without the introduction of moisture. A variant of the method utilises the adhesive in the form of paper impregnated with glue solution. This system is of particular interest in connection with veneering and plywood making.

(*d*) *Application by the Two-solution Process.*—This method is adopted in cases where the adhesive solutions are not very stable and where the strength and resistance to degluing of the dried film are to be increased by hardening or insolubilisation with or without the application of heat.

It is used mainly with casein and rubber adhesives, etc. The procedure is as follows :—The materials which give the desired interaction are divided between the two solutions. As an example, a rubber solution is divided into two parts, one of which contains the sulphur and the other the vulcanisation accelerator ; the solutions are mixed just before use. This process can be modified as follows :—Each of the surfaces to be joined is coated with one of the above-mentioned solutions, the reaction taking place when the two surfaces are brought together in the actual joining process. A third modification consists of adding the insolubilising agent in a modified form, such that it has no effect in the cold but exerts its influence only when heat is applied at the moment of using the adhesive. For instance, formaldehyde solution rapidly insolubilises gelatin. If, however, the formaldehyde be added to the gelatin in the form of hexamethylenetetramine, the active formaldehyde is not set at liberty until heat is applied, in the veneer presses, etc.

(*e*) *Application by Spraying.*—This method is of interest only in exceptional cases where the surface to be treated is very extensive and where the use of gumming machines is for one reason or other impracticable. It is obvious that only solutions of comparatively low viscosity are suitable for application by this method. On the whole, the complexities and drawbacks of the method are such that, in the author's experience, very serious consideration should be given to the possibilities of alternative methods before a final decision to use the spray method be taken.

(*f*) *Application by Gumming Machines.*—A gumming machine consists essentially of a tank containing the adhesive solution, a system of spreading cylinders (the excess of paste being removed by rolling with subsidiary cylinders or by scraping with a " doctor knife ") and

an endless cloth band upon which the gummed sheet is collected and from which it is removed. In large installations where the paper gumming process functions continuously, the plant is completed by the provision of a drier and winding drum for the finished coated sheet. The gumming machine, which is, of course, suitable for the application of most kinds of cold adhesive, has not received as yet the measure of industrial adoption which its utility would seem to warrant.

(*g*) *Application by the Use of Entirely Automatic Machines.*—A description of the mechanism of this type of plant hardly seems called for here. Some of the modern installations are marvels of mechanical ingenuity but, as in the case of the simpler gumming machines, it is doubtful whether industrialists as a whole have as yet fully appreciated their worth.

CHAPTER II.

THE MECHANISM OF ADHESION.

Chemical Considerations.—Since this book has been written not so much for professional chemists as for the broad mass of makers and users of industrial adhesives, it may not be considered superfluous perhaps to discuss, on very elementary lines, those aspects of chemistry which have a direct bearing on the industry.

The study of chemistry is usually divided into two broad divisions, inorganic and organic. The former covers, generally speaking, all the elements, other than carbon, and their compounds, whilst organic chemistry is concerned essentially with the study of the often complex compounds of carbon.

It was for long thought that the carbon compounds, with the exception of such simple materials as carbon dioxide and the carbonates (which for the sake of convenience are usually considered under the heading of inorganic chemistry), required the intermediation of some "vital factor" in their formation, and it was not until Wöhler in 1828 succeeded in preparing urea, hitherto solely obtained as a product of animal metabolism, from purely inorganic materials, that it was recognised that the doctrine of "vital force" could not be maintained.

To-day, of course, thousands of important organic compounds are manufactured by synthetic methods from inorganic materials. Owing, however, to the enormous number of carbon products, to the fact that many of the most important materials have not yet been found capable of synthesis, and to a number of peculiarities associated with the chemistry of carbon, organic chemistry is still kept as a distinct branch of the science of chemistry.

So far as the adhesives industry is concerned, inorganic chemistry furnishes the materials employed as agents for the transformation of the colloidal adhesive materials themselves, these latter being mostly organic products.

The whole of the material which forms the substance of this earth is composed fundamentally of some 92 chemical elements, alone or, more usually, in combination. Although researches in radioactivity and physics during the past thirty or forty years have shown that

the atoms themselves are essentially composite materials built up of different numbers and arrangements of one basic constituent, the electron, nevertheless, with the exception of certain rare elements of the radioactive type, which slowly undergo spontaneous decomposition, the atoms are highly resistant to any attempt to break them down or to convert them into atoms of other elements.

For all practical purposes then, the atoms are the fundamental units of chemistry. For the most part they possess the property of combining with fellow atoms of similar kind to form molecules of the simple elements, or with atoms of other elements to form compounds.

The simple bodies can be classified broadly into metals and non-metals. The combination of a non-metal with oxygen gives an oxide which, usually, possesses acid-forming properties. The oxide of a metal on the other hand, possesses basic properties. Acids and bases are mutually opposite products which, when brought into contact, combine with the formation of new bodies, or salts, with the simultaneous liberation of water.

The principal inorganic chemicals and chemical materials which interest the adhesives industry are :—

The acids (sulphuric acid, nitric acid, hydrochloric acid).
The bases (caustic soda, lime, potash, etc.).
The salts (sodium chloride, sodium sulphate, etc.).

The type of reaction which occurs between an acid and a base or alkali is one which is very frequently made use of in preparing adhesives.

Many chemical products and elements can also be grouped broadly into oxidising agents and reducing agents. The former have the property of transferring, directly or indirectly, oxygen to other materials. The oxidising power of oxygen itself as evidenced, say, in the rusting of iron, is direct; whilst the use of chlorine compounds in bleaching is an instance of indirect oxidation, since the chlorine compounds react with water, which must also be present, to form oxygen, which is in all cases the active oxidising material. The reducing agents are opposite in action to the oxidising agents, typical reducing agents being hydrogen and salts such as sodium sulphite. In any oxidation process, of course, the material being oxidised may be considered as a reducing agent.

The above concepts, of course, are presented in but the sketchiest lines, and the reader interested is referred to any of the numerous good books available on elementary chemistry.

Before discussing from the standpoint of the adhesives industry

the control of the neutralisation of acids by alkalis, it should perhaps be pointed out that the chemical reactions between acids and bases or between oxidising and reducing agents are sometimes accompanied by the liberation of heat (exothermic reactions) or by the absorption of heat (endothermic reactions). In the former case, the energy content of the compound formed is less, naturally, than that of the simple materials from which it was formed. In the latter case, the reverse holds true.

Control of Acidity.—In practice, neutralisation reactions between acids and bases are followed and controlled by the use of "indicators," these latter being materials (natural or synthetic dyestuffs or allied materials) the colour of which is dependent upon the acidity or alkalinity of the medium in which they find themselves. The ordinary "indicators" are litmus, methyl orange and phenolphthalein. The first-mentioned is red under acid conditions and becomes blue-violet as soon as the medium in which it finds itself changes to the alkaline state. Methyl orange is red in acids and yellow in alkalis, whilst phenolphthalein is colourless under acid conditions but assumes a rich red coloration immediately the slightest excess of free alkali is present.

To-day, the range of "indicators" is very extensive, products being available which change colour not only on the transformation of solutions from actual acidity to alkalinity but also with changes in the degree of acidity or alkalinity of the materials. In fact, the control of "acidity conditions" in industrial operations has now become a fine art.

For the needs of the ordinary maker and user of adhesives, however, litmus or, in some cases, phenolphthalein is quite satisfactory. Litmus solutions can be secured in small or large quantities from any laboratory furnisher. Instead of the solution, litmus papers, readily prepared, are more conveniently employed. It is advisable to prepare two lots of litmus paper, as follows:—The litmus solution is divided into two parts. One is stirred with a glass rod, the end of which has been touched with a little ammonia, and the other is stirred with a glass rod which has been dipped into hydrochloric acid. The first part of the solution becomes definitely blue and the second bright red. Filter paper is dipped into the solutions and, after drying, cut into small strips. For control of acidity conditions in adhesive manufacture, these litmus papers are far more practicable than litmus solutions.

As adhesive preparations are always more or less viscous liquids, their effect on litmus paper is much slower than in the case of thinner liquids, particularly as the point of neutrality is approached. Consequently it is advisable to soak the litmus paper in water before

use, and to increase the time of contact. The way in which the test should be carried out is as follows: Two strips of litmus paper, one red and one blue, are held in the left hand and dipped into water. With the right hand, a clean glass rod is dipped in the adhesives solution and the two strips of litmus paper rolled round the rod by rotating the latter. If the paste being tested is either distinctly alkaline or distinctly acid, the colour change takes place fairly rapidly, but when near the point of neutrality the change takes place slowly, probably not until after a few minutes, during which the rod should be placed at the edge of the working bench with its treated portion jutting out. By testing in this way, perfectly reliable results are obtained when controlling either laboratory or plant operations.

Colloids.—Inorganic chemical products have usually, though not invariably, well-defined physical properties. In most instances they can be obtained in the form of crystals, and are consequently termed "crystalloids," to distinguish them from a large number of organic products which have inconstant and indefinite physical properties and which are termed "colloids." It should be noted that crystalloids are also met with among organic chemicals (for instance, ordinary cane sugar), whilst the property of forming colloids is shared by certain inorganic products such as silica gel and the colloidal clay or bentonite which will be referred to later. On the whole, however, crystalloids are essentially inorganic compounds and the colloids essentially organic compounds.

All the organic products utilised as commercial adhesives, whether of vegetable or animal origin, fall into the group of colloids. No very concise definition can be given of the word "colloid." The term is applied to materials which possess properties which are the exact opposite of the properties possessed by crystalloids. Colloidal solutions are not true solutions. They are always more or less unstable, the product being held in suspension in the dispersed state in the form of large molecular complexes which are sometimes termed "micellæ." The colloidal state is in some respects intermediate between the liquid and solid states.

Owing to the relatively large dimensions of the micellæ, colloidal solutions are not capable of dialysis; that is, when they are placed within the confines of a semi-permeable membrane such as a collodion membrane, the dispersed material does not pass through the membrane. With a solution of a crystalloid, such as salt or sugar, the dissolved body will pass through the membrane.

Another characteristic of colloidal materials is their possession of a certain flexibility and plasticity, properties not shared as a rule by the crystalloids. Colloidal solutions, in general, possess rather

a high viscosity. For the sake of abbreviation, a colloidal solution is called a "sol." If water is the medium it is called a "hydrosol," if alcohol is the medium an "alcosol" and if an organic solvent is the medium an "organosol."

By coagulation or gelatinisation the sols give rise to "gels." For instance, neutralisation by hydrochloric acid of a solution of sodium silicate, in suitable concentrations, causes the mass to set solid owing to the formation of "silica gel." These gels almost always contain absorbed liquid, and the phenomenon whereby this liquid is liberated from the gels is called "syneresis." For instance, in the example just given, the entrained water tends to separate fairly rapidly from the silica gel. This phenomenon of syneresis is furthered by low temperature and is a point always to be borne in mind when considering the storage or transport in winter of certain vegetable base adhesives which have a tendency to gelatinise.

One of the most important modifications in the properties of material which result from conversion into the colloidal state is the enormous increase which is occasioned in the active surface of the material. All solid substances possess the power to a greater or less degree of adsorbing gases or liquids on their surfaces. This adsorption (which should not be confused with absorption as, for instance, the absorption of ammonia by water) is a phenomenon of molecular attraction between the adsorbed material and the surface which acts as the adsorbing agent. The adsorption process is very largely a physical process. Subsidiary chemical affinities between the molecules may be, and probably are, involved but adsorption is accompanied by no chemical change in the ordinary sense of the word.

The phenomenon of adsorption is a distinctly important one in connection with adhesives. Its magnitude is directly dependent upon the areas of the surfaces involved. That is why conversion of any material to the colloidal state involves a very great increase in its adsorptive properties. For instance, a piece of gum arabic in lump form has not a very extensive surface and the phenomena due to surface action are slight. If this lump of gum is now treated with water to produce a colloidal suspension, the surface area of the material is increased enormously, with a corresponding increase in the magnitude of the surface reactions. From this it follows that the stickiness of adhesive solutions increases as the degree of dispersion of the adhesive in the colloidal solution increases. For instance, a starch paste simply hydrolysed, that is, simply heated with water, gives a gelatinous solution capable of absorbing a large mass of water, but does not produce a good adhesive, the reason being that the starch is insufficiently dispersed in the water, the micellæ merely being

swollen. By appropriate treatment of the starch the degree of dispersion can be steadily increased and the value of the material as a glue consequently enhanced, until finally, a high strength glue is obtained in which the degree of dispersion of the starch is as high as possible.

This transformation of gelatinising power into sticking power is accompanied by a reduction in thickening properties. Further, the density and consequently the percentage of dry matter having become greater, there will remain after drying a film sufficiently dense to avoid too great a degree of shrinkage, to fill in interstices and inequalities in the surfaces being joined and thus to increase the actual area of contact between the two surfaces.

The force which binds all materials is a phenomenon of molecular attraction by intimate contact. According to this view it would seem that if we broke a plate, accurately fitted together the broken portions and subjected them to very high pressure, there should be perfect jointing and the plate should be as good as new. In practice, of course, this does not happen, the reason being that the surfaces formed by the break immediately adsorb thin layers of air, these layers preventing the reunion of the materials even under the highest pressure.

What happens when colloidal adhesive solutions are used is that these latter, by their high adsorptive powers, tend to fix themselves on the solid through the layer of air.

Surface Tension Considerations.—The surface affinities, and consequently the impregnating properties, of colloidal adhesive solutions cannot only be enhanced by raising the degree of dispersion of the colloid but also by the addition of what are known as dispersing, emulsifying or wetting-out agents. These latter terms are used somewhat indiscriminately according to the purpose for which the material is to be used, but the materials all possess the outstanding and specific property of lowering the surface tension of solutions to which they are added.

The existence of surface tension and its reduction by the addition of other materials can be instanced by the following simple test: If a flat surface, say a sheet of glass, is wetted with water and a small disc placed on top, it will be noted that an attempt to lift the disc encounters a very definite resistance. By the aid of suitable apparatus, this resistance can be determined and gives a measure of the surface tension of the liquid (water). The addition of a little soap to the water will be found to be accompanied by much lessened resistance when the disc is lifted. Very small quantities of soap are sufficient.

Another observation which bears out this point is that if one's

hands are clean and free from oily matter it is very difficult to wet them rapidly with pure water, but perfectly easy to wet them if the water is a little soapy.

Soap is the usual and cheapest wetting-out agent in aqueous adhesives but, as will be shown later, many of the numerous members of this group of products which are now available can be very usefully employed in these adhesives with the object of facilitating their adherence to the surfaces to be joined and of overcoming any deficiency in affinity which these surfaces may possess for aqueous solutions.

With a cold adhesive in aqueous solution, containing a suitable wetting-out agent, a varnished surface, for instance, can be readily coated, whilst the same solution, but containing no wetting-out agent, will not spread and when an attempt is made to coat the varnished surface the adhesive will simply form localised blobs.

The wetting properties of certain adhesives may also be secured and amplified by the addition of hygroscopic or plasticising agents, but it should always be borne in mind that when these latter materials are employed both the rapidity of drying of the adhesive and the hardness of the film produced are reduced.

Viscosity.—To produce a joint of maximum strength, the viscosity of an adhesive solution, although this is dependent to some extent upon the nature of the surfaces being joined, must fall between certain definite limits. If the solution is too viscous, in other words if the adhesive material is insufficiently dispersed, the solution will be deficient in wetting power or, what is the same thing, lacking in power of anchoring itself to the surface being coated. An anhydrous adhesive it should be noted has virtually no sticking power at all, and the belief which is still fairly generally held among users of adhesives that the thicker the paste the better will be its behaviour in use is quite fallacious. If, on the other hand, the adhesive solution is not viscous enough, when applied to any but the least absorbent types of material it will, unless used in undesirable excess, tend to be more or less absorbed by capillarity through the pores of the material.

The addition of emulsifying agents will impart wetting power to adhesive solutions which are lacking in this property, particularly with highly concentrated adhesive pastes. This is a useful expedient where it is necessary to use solutions that are very viscous. Too high a degree of fluidity can be countered by the use ot formulæ which give rise to products combining high viscosities with high dilutions, or by the addition of thickening agents which function simply as fillers and supports. In some cases, also, solutions which are on the

thin side can advantageously be applied in two coats, the first coat after drying being virtually a non-permeable surface upon which the coat which is to act as the actual adhesive is placed.

Influence of Atmospheric Pressure.—In addition to the surface actions which have just been discussed, there is another factor, if a subsidiary one, which always comes into play when adhesives are used, and this is the influence of atmospheric pressure. A certain difficulty is always experienced in the attempt to separate two well planed and perfectly cleaned surfaces, two sheets of glass for example. A pull at right-angles to the direction of the joint between the two pieces of glass will tend to create a vacuum between the two surfaces and the resistance experienced is due to the counterbalancing force of the pressure of the atmosphere. This phenomenon is considerably amplified if the two sheets of glass are moistened, the water in this case acting as a bonding agent or as an "adhesive."

All the principles of adhesive action fall within the topics just covered, and these should always be considered in the formulation of industrial adhesives.

Catalysis.—"Catalysis" is the term given to the acceleration of the speed of chemical reaction due to the presence of very small quantities of other substances—termed "catalysts"—which substances do not themselves play any chemical part in the reaction or, if they do, are substantially unchanged at the end of the process. The great majority of catalysts are very susceptible to the influence of traces of foreign substances. In some cases these substances act as "poisons" to the catalysts and slow up, if they do not actually stop, the reaction. In other cases these substances may have exactly the opposite effect and by their presence activate the catalyst or protect it from the influence of poisons.

Practically every known element or compound is capable of functioning as a catalyst for one or more reactions. In industry the metals or their oxides find the widest application. For instance, copper or silver is the catalyst used when oxidising methyl alcohol into formaldehyde, and the iron oxides are used as catalysts in some of the processes for the direct manufacture of ammonia by the combination of nitrogen and hydrogen under high temperatures and pressures. As an instance of the use of salts, there is the employment of mercuric sulphate in the process of making acetaldehyde, later to be made into acetic acid, from acetylene. In sulphuric acid manufacture by the ordinary chamber process the oxides of nitrogen are the catalysts used. So far as the adhesives industry is concerned, however, the alkalis are the materials which are mainly employed for their catalytic influence. An instance is the employment of

sodium bicarbonate in the production of high-strength pastes from starch.

Catalysts also play a very important part in vital processes, that is, the processes going on in the growth and development of both animals and plants. One group of such products is comprised of the "diastases," materials influencing the conversion of the starches into sugars. The activity of these biological catalysts is in general higher than that of the inorganic catalysts. They function in exceptionally small concentrations, but suffer from the drawback that they are more susceptible to the paralysing activities of "anti-ferments" than are the inorganic catalysts to poisons. They are also more sensitive to temperature conditions, whilst their activity falls off more markedly with the passage of time. In the adhesives industry these biological catalysts find use in certain processes for the conversion of the starches into the dextrins.

CHAPTER III.

THE SIMPLE TESTING OF ADHESIVES.

It is not proposed in this chapter to describe any elaborate testing methods involving the use of special and complicated apparatus but rather to discuss simple and direct methods of carrying out comparative trials. An adhesive for application either by the hot or the cold process is of interest in two stages; firstly, as the more or less viscous solution in which it is originally applied, and secondly, as the dried film in the form of which it cements the two surfaces which are to be joined. Accurate positive measurement of the properties of adhesives necessitates both scientific knowledge and manipulative skill. For the ordinary maker and user of cold adhesives, however, all that is necessary is simple comparative testing that can be carried out speedily and with the minimum amount of apparatus.

Apparatus Required.—The equipment necessary for this work is an analytical balance (which need not be very sensitive, since lack in sensitivity can be made good by weighing out larger quantities of materials), four graduated burettes (three of 50 c.c. capacity graduated in cubic centimetres and one of 100 c.c. capacity), a few flat-bottomed lipped porcelain dishes, test-tubes and a test-tube stand, a small hot-plate heated by gas—more useful than a Bunsen burner—some glass rods about 18 cm. long and about 7-8 mm. in diameter to mix the viscous solutions, a water-bath, sand-bath, desiccator, drying oven, and the necessary chemical and indicator solutions.

The graduated burettes are used for the determination of the acidity or the alkalinity of the solutions, using a few drops of litmus solution or phenolphthalein solution as indicator—or for the rapid addition of measured volumes of solutions of the various reagents to the experimental batches. The 100 c.c. burette, for instance, is employed mainly for the addition of the water to the batches. One of the 50 c.c. burettes is filled with standard alkali solution for the determination of acidity in adhesive solutions and the other with standard acid solution for the determination of alkalinity. The test-tubes will be used chiefly to examine the effect of the addition of new

constituents to adhesive solutions. If turbidity, or actual precipitation, is seen to occur in such a case, the proposed addition is generally, though not always, undesirable.

In carrying out comparative tests, the best plan is to prepare a bulk solution on which the effect of the addition of various substances can be tried. Equal volumes of such a solution can be measured out into a number of the porcelain dishes and treated with progressively increasing volumes of the product the effect of which is under investigation. Similarly, in test-tube work it is often possible to carry out 30 or 40 hydrolytic operations at the same time by immersing the tubes in the same bath of boiling water. As in all experimental work the main point to be borne in mind, of course, when carrying out trials on cold adhesives, is to vary only one factor at a time.

The Viscosity of Adhesives.—The principal properties to be investigated in solutions of cold adhesives are their viscosity and the degree and nature of their departure from neutrality. In the writer's experience the best viscometer is useless in this work, and as a concrete example of the method he has found best, he gives the following: A maker of starch or dextrin adhesives is desirous of securing a fresh supply of raw material. He looks into the market position and secures about ten samples from different sources of supply. These samples are made up into small batches, whilst an eleventh batch is made up with the starch or dextrin currently used in his process. Inspection of the various experimental batches will, after a certain amount of experience, allow him to select immediately the best raw material not only from the viewpoint of viscosity but also from those of colour and price. It is recommended that the experimental batches, made up in the porcelain dishes, be not less than 90 to 100 grammes. This quantity gives a surface adequately extensive to allow of viscosity examination by stirring with a glass rod, etc. With smaller batches, again, slight errors in weighing are apt to assume too great importance.

The significance of the test for viscosity will be discussed later for each class of raw material, but since the starches and the dextrins, the most important group of raw materials, have just been mentioned, the following important points may just as well be brought to the attention of the reader here:—(*a*) The starch-derived adhesives tend either to become fluid or to thicken on standing. (*b*) They tend to thicken by reversion, this being accelerated by the more highly concentrated nature of their solutions.

It should never be lost sight of that these starch or dextrin solutions are not wholly true solutions, but are, rather, colloidal solutions, or more accurately, emulsions or suspensions of micellæ

more or less swollen and more or less dispersed in the intermicellar liquid. These solutions are consequently liable to lose their viscosity by fermentation or by the attack of dissolved constituents, or they are liable to coagulate or "revert" by the rupture of the emulsion. For this reason test solutions should not be examined for their viscosity until they have had the opportunity to become stabilised —usually standing overnight at ordinary temperatures is sufficient.

Acidity or Alkalinity of Adhesives.—The alkalinity or the acidity of a sample of adhesive solution is easily determined by simple titration. If the paste is an alkaline one titration is effected with a dilute solution of hydrochloric acid the strength of which is known. Ten grammes of the paste under test are weighed out into a porcelain dish and diluted with two or three times their volume of water to reduce the viscosity. A few drops of fresh litmus solution are then added as indicator, the acid then being run slowly from the burette into the porcelain dish, the contents of the dish being kept well stirred with a glass rod. The addition of the acid is stopped immediately the colour of the solution in the dish changes from a distinct blue to a violet-red. If the colour is distinctly red, rather too much acid has been added and the titration should be repeated, greater care being taken when the end-point is being approached. The volume of acid that has been added from the burette is read off, the actual weight of acid used is calculated, and this converted into terms of alkali gives the free alkali content of the paste under test. Phenolphthalein, which is colourless in acid solution but turns deep red in the presence of alkali, is a better indicator than litmus in some cases.

If the original paste has an acid reaction, the titration is carried out in the same way, but in this case the burette contains a dilute standard solution of caustic soda.

Normally, very few cold adhesives are truly neutral. They almost always possess a more or less pronounced acid or alkaline reaction introduced deliberately in their formulation to assure better stability and adhesive power. The free acid or alkali not only improves the properties of the adhesive solution itself but is of benefit indirectly by its effect in slightly etching the surfaces which are to be united by the paste. Most of the materials to which adhesives are applied in industry can withstand the action of small quantities of acids or alkalis without adverse effect. Where it is suspected that such traces may be harmful, trials can be carried out with the adhesive on the material. It should always be remembered, though, that perfect neutrality always tends to reduce the adhesive powers of a paste.

Examination of the Films.—In the comparative examination of the dry films produced by cold adhesives, similar simple tests are offered by the writer as quite suitable for the ordinary maker and user. With the exception of adhesives for application to wood, the main criterion of which is capability of forming mechanically strong joints, the properties of the dried film can most conveniently and logically be tested on the film itself, spread for experimental purposes on a glass sheet.

With a little experience and capacity for making deductions, quite sound conclusions as to the adhesive value of the film can be drawn from simple inspection of the dried film.

Resistance of the film to tensile pull is a corollary of the hardness of the dried film, a property which can be measured by scratching or scraping the films of the various samples under comparative test. It is necessary, of course, that the films be prepared under exactly the same conditions; in other words, the paste should be spread on the glass in the same way and the various samples dried at the same temperature and under the same atmospheric conditions. In the case of water-soluble adhesives, the adherence of the film to glass will be the greater the more dispersed the condition of the actual adhesive substance, and will be greatest, consequently, when the solution is a true one. With a good adhesive, it is often found that, on scraping the film, a thin layer of the glass itself is actually scaled off, a positive indication of the impregnating power of the solution and of the strength of the film being greater than that of the glass. In the case of cold adhesives which are solutions in organic solvents, the film test method is slightly different.

Comparative examination of the resistance to separation ("degluing") of the dried films of cold adhesive is effected quite simply by sticking strips of paper coated with the various solutions under test to a sheet of glass, immersing the glass sheet in water and examining the degree of resistance which the various paper strips offer to pulling off. Useful indications are also given in this direction by immersing glass sheets, upon which the adhesive films have dried, in water and noting the degree to which the film swells and the degree of ease with which it softens (by scraping tests).

Quantitative comparative figures on the degree of swelling undergone by the film on immersion in water can be obtained by weighing the coated glass sheet prior to immersion, immersing in water for, say, 24 hours and then weighing again after draining. It is important, of course, if reliable comparative results are to be obtained, that all the sheets be subjected to identical treatment both as to method and time of draining.

A further method of measuring the moisture resistance, and consequently resistance to detachment, of an adhesive film is to produce the film on a surface, such as an oily surface or a celluloid surface, from which it can readily be detached and then to transfer it to a glass ring so that it forms a little pouch. This pouch is then filled with water and the time taken for the water to percolate through the film is noted. It is, however, not quite so easy to obtain really comparative results by this method.

In adhesives of the hydrosol type the speed of drying is a function of the percentage of moisture originally present in the film and of the nature and quantity of any hygroscopic materials that may be present. In adhesives of the organosol type the speed of drying is directly dependent upon the speed of evaporation of the solvent or the mixture of solvents used.

When carrying out drying time trials with either type of adhesive solution, the essential point is to keep the coated glass sheet in a place protected from air currents. Provided reasonable uniformity has been observed in the method of spreading the adhesive sample on the glass sheet, this simple method of carrying out drying time tests gives perfectly satisfactory results.

In making starch-derived adhesives it is advisable, as will be seen later, sometimes to incorporate products of a hygroscopic nature, and the drying time test can be employed to examine this factor only. In a test of this kind small batches of the paste varying from one to the other by the addition of gradually increasing amounts of the hygroscopic material would be made. The pastes would then be coated on glass sheets and the films allowed to dry at ordinary temperature under identical conditions. The point at which the further addition of hygroscopic agent occasions an appreciable slowing-down in the rate of drying of the solution can readily be ascertained.

As this question of the content of hygroscopic material is important, it is advisable to check the results obtained above by what may be termed a " counter-test." In this case all the test films on their glass sheets are dried to completion in the air, and are then placed under a large glass receptacle the side walls and bottom of which have been moistened. Inspection of the behaviour of the samples will readily show those which most easily absorb moisture from the surrounding atmosphere. Too rapid moisture re-absorption is always an undesirable feature in cold adhesives, except in those cases where the paste is to be used to agglomerate powders, as in the manufacture of wallpapers.

The necessity for rapidity of drying and the production of hard non-hygroscopic films is particularly great in adhesive pastes that

are to be used on metallic surfaces, for instance the sticking of labels or wrappers on tinplate or aluminium boxes, since the longer the paste remains in the moist condition the greater is the danger of oxidation of the metal or of other undesired chemical or physical changes taking place in the zone between the paper and the metal surface. With two starch adhesives, for instance, the one neutral but rather hygroscopic and the other slightly basic but drying more rapidly, it is the former which is far more likely to give rise to oxidation troubles.

A case of this kind is met with in one of the dextrin adhesives which will be discussed later. This adhesive paste (Formula B-2) is of a pronouncedly basic nature but is satisfactory as regards speed of drying, and an adhesive of this type is particularly well suited for pasting the paper wrappers on tinplate biscuit tins. The basic dextrin adhesive in this case not only functions as an efficient adhesive, but acts as a protective layer for the metal of the box.

It should never be overlooked, of course, that adhesives, with their manifold and varied uses, furnish one of the most difficult subjects upon which to generalise, since nearly every use constitutes a particular case of its own. At the same time, it is the writer's experience that the broad generalisations he has given are in the majority of cases correct.

The tendency of a dried film to crystallise, if such tendency is suspected, is best confirmed by keeping the dried film for some days after the drying time results have been obtained. Any excess of solids will reveal themselves as a very fine layer forming along the surface of the film. Crystallisation is a defect most likely to be encountered in the starch adhesives, and is accompanied by a reduction in the strength of the film.

The properties of a dried film as regards plasticity and flexibility can be examined directly by allowing a sample of the adhesive to dry on a perfectly flat surface to which the film will not adhere. A sheet of glass thinly coated with oil, a sheet of celluloid (which may also be coated with oil) or, better still, a sheet of bakelite or nickel-plated or enamelled metal can be used for this purpose. After drying, a very thin sheet, matt on the side exposed to the air, and polished on the side which touches the supporting surface, is obtained. The film is detached, cut into narrow strips, and examined by repeated bending along the same fold. The film produced by a " strong glue " should not be brittle, friable or pulverulent, but should be hard and tough, particularly where it is to be used for joints that have to withstand considerable stresses or vibration.

In regard to these " strong glues," it should be noted that if the

adhesive possesses a crystalloidal tendency—as do gum arabic and dextrin adhesives—this characteristic tends to become more pronounced as the joint made is subjected to stress, with the result that the film acquires a powdery nature. With a film of flexible colloidal nature this change under vibration stress does not occur. Consequently, in the production of high-strength cold adhesives the obviation or minimisation of any tendency to granulation is a point to be watched. For instance, in the process for the production of high-strength cold adhesives of the starch type for use as substitutes for casein adhesives (to be described later), the product after the initial treatment with alkali, oxidising agent and catalyst possesses a certain tendency to granulation. This tendency is then removed by the addition of an appropriate solvent, etc., as will be shown.

Film clouding is a trouble usually experienced only with solutions of cellulose esters or rubber in organic solvents, the reasons being discussed in detail in the appropriate chapter. In this case there is no need to use glass sheets to examine the nature of the film, glass rods being quite suitable. To take a concrete example, supposing we want to find just how much butyl alcohol is to be added to a certain cellulose solution to prevent the film clouding during the final stages of the evaporation of the solvents, we proceed as follows: To the original solution a measured small amount of butyl alcohol is added and well mixed in with a glass rod. The glass rod is removed and laid at the edge of the table with its coated portion projecting. A second addition of butyl alcohol is now made and the second rod used is placed at the side of the first one. In this way a whole series of rods is laid out. The best quantity of butyl alcohol to use is that in the mixture which coats the rod which occupies the intermediate position between the one on which the film has dried with pronounced clouding and the one on which the additional amount of butyl alcohol has apparently produced no further effect.

Adhesives for Wood.—The testing of adhesives which are to be used in connection with wood presents a special case. With adhesives for paper, cardboard, cloth, etc., it is a relatively easy matter to select the best type of material, but when, as in wood glues, high mechanical strength is the paramount factor, the testing methods are not so simple. Whatever the methods used, the results obtained are very imprecise, but a reliable approximation can be reached by taking the mean of a number of determinations.

The simplest testing method is the empirical one often used in joiners' shops and by cabinet makers. Two pieces of wood are glued together and after drying separated by blows with a hammer. If the wood breaks along a plane other than the joint, or if it breaks along

the joint but with splinters of wood firmly attached to the glue, the glue is considered a good one, a conclusion with which it is impossible to quarrel.

A more scientific, though more complicated and costly testing method, is that which makes use of the dynamometer. The wooden test pieces are smoothed and planed cubes of sizes as nearly identical as possible. The adhesive under test is spread as uniformly as possible and under constant temperature conditions and the joint is made between two cubes under standardised conditions as regards pressure of application and time of drying. Slices are then sawn off the double cube in a direction at right-angles to the glued joint and pulled apart by the jaws of the dynamometer, the force required to produce rupture being measured on a graduated lever or on a dial. A number of such tests is put through, one after the other, and the mean is taken of the various readings on the instrument. The results are more positive if the dynamometer is actuated not by hand but by a small electric motor. In this manner the stress up to break is applied regularly and uniformly.

Standard Tests.—So far as ordinary glues are concerned, whether in cake form or as liquid or jelly, methods of testing that have secured general agreement have been published recently by the British Standards Institution.[1] These methods have been drawn up by a special Committee upon which, in addition to Government Departments and Scientific Organisations, the following Industrial Organisations were represented: The Paper Makers' Association, The British Furniture Trades Joint Committee, The British Paper Box Manufacturers' Federation, The Federation of Hide Gelatine and Glue Manufacturers, and The Master Bookbinders' Association. The Specification gives details of numerous tests which represent the experience of the trade over many years, and among others a method is given for the determination of joint strength in shear of glued wood. Many of the tests, of course, are considered mainly from the viewpoint of ordinary hot glues, but the document is of decided interest to makers and users of usual types of cold adhesives. The methods given are, however, of a somewhat different degree of accuracy than the methods outlined in this Chapter, which it must again be stressed are offered only as a guide to the maker and user in carrying out comparative tests with the simplest possible equipment and in the shortest time possible.

[1] British Standard Methods of Testing Glues (Bone, Skin and Fish Glues) No. 647, 1935, published by The British Standards Institution, 28 Victoria Street, London, S.W. 1, price 3/8 post free.

CHAPTER IV.

RAW MATERIALS.

THE most convenient and useful method for the classification of the numerous types of adhesive solutions used in industry is that based on the raw material utilised, always bearing in mind the fact that more than one of the main groups of raw materials may be employed in a single adhesive. The main groups of raw materials are the following:

Raw Materials of Animal Origin.

(1) Gelatin (extracted from bones, hides, skins, sinews, etc.).
(2) Isinglass and fish glue (extracted from swimming bladders, bones and scales, etc. of fish).
(3) Casein (extracted from milk).
(4) Albumin (extracted from egg white and blood).

Raw Materials of Vegetable Origin.

(5) Water-soluble gums (gum arabic, gum tragacanth, gum senegal, etc.).
(6) Water-insoluble gum resins (ordinary rosin, gum lac, etc.).
(7) Gum elastics (rubber, latex, gutta-percha, etc.).
(8) Algæ.
(9) Flours and starches.
(10) Dextrins.
(11) Lime sucrate.
(12) Waste lyes from sulphite pulp manufacture.
(13) Synthetic resins.
(14) Cellulose (cellulose nitrate, cellulose acetate, etc.).

Raw Materials of Mineral Origin.

(15) Sodium silicate.

The actual production of these various raw materials will not be considered in any great detail, since it is not a matter that concerns

very closely the maker and user of adhesives. What are considered to be the essentials will, however, be briefly discussed. Some of the raw materials in the foregoing list are but of minor interest, since better and cheaper adhesives can usually be obtained by the adoption of other materials in their place.

Raw Materials of Animal Origin.

(1) **Gelatin.**—Gelatin as such does not exist in nature, but is the result of the hydrolytic action of hot water or steam under pressure on collagenic materials. Even to-day considerable uncertainty exists as to the real nature and physical properties of gelatin, although the position is gradually being clarified. The reader interested in this aspect of the matter is referred to the work of the late Professor S. B. Schryver, the results of which are summarised in the Third and Final Report of the Adhesives Research Committee of the Department of Scientific and Industrial Research.[1] For our immediate purposes it may be taken that gelatin is composed principally of glutin, or gliadin as it is now more frequently termed, and chondrin, the former being the really important constituent of pure gelatin.

The distinction between the gelatins and the glues is not very precise. The term "gelatin" is understood commercially to cover a very pure glue supplied as thin sheets, colourless or of very pale colour, possessing a high gelatinising power but comparatively poor agglutinant properties. By "glue" is understood an impurer type of material, deeper in colour, with less thickening power but with a greater degree of dispersive efficiency. The usual type of glue is represented by the well-known joiners' glue.

The raw materials and the methods of working them up are the same whether gelatin or glue is the desired end-product. If gelatin is to be made, however, the raw materials are selected more carefully and greater precautions to secure freedom from impurities, etc., are taken during the manufacturing process. In all cases, however, methods which do not necessitate too prolonged hydrolysis are selected since otherwise the quality of the glue or gelatin would suffer from the too profound degradation of the molecule.

There are three principal methods of extraction: (i) Direct extraction of the skins, cartilages, tendons, etc., by treatment with hot water. (ii) Where bones are employed as the raw material, these are first demineralised by the action of an acid, usually hydrochloric acid, and the cartilaginous material or "osseine" remaining is then hydrolysed. (iii) The raw material is treated with steam under

[1] Obtainable from H.M. Stationery Office, London, price 2/6 net.

pressure in a battery of extractors employing the counter-current principle. In this system the fresh bones entering at one end of the battery encounter liquor already nearly fully charged with extracted matter, the bones from which most of the organic matter has been removed meeting the fresh pressure steam at the other end of the extraction battery. This method, it will be appreciated, means economy of steam, thorough extraction of the bones and the production of gelatin liquor of high concentration. In principle, the best glues, and particularly the best high-grade gelatins are made by the second method.

The gelatins swell strongly in cold water but do not go into actual solution until the temperature is raised.

(2) **Isinglass.**—Fish glue is an excellent raw material for adhesives making, but its disadvantages are its high price and its odour. The true isinglass is extracted from the swimming bladder of the sturgeon. Fish glues of somewhat lesser value are extracted from the cartilage, skins and heads of fish and even, although in this case they hardly merit the description fish glues, from the intestines of goats or sheep. A substitute for fish glue has also been made from blood fibrin.

Fish glues, other than true isinglass, have never enjoyed the high reputation of glue made from the hides and bones of land animals on account not only of their disagreeable odour but also because of their tendency to absorb moisture. It is worth noting, though, that a method of producing from fish skins odourless and non-hygroscopic glues which compare favourably with high-grade animal glues in adhesive power has been worked out by Dr. J. C. Kernot, whose work is described in the Second Report of the Adhesives Research Committee of the Department of Scientific and Industrial Research. This process has been worked on the commercial scale, but whether it is being operated to-day is uncertain.

In the manufacture of isinglass the membranes of the swimming bladders of the sturgeon are treated with hot water. The yield is high, usually about 90 per cent. The liquors are deodorised and decolorised, concentrated, poured into moulds and dried. In contradistinction to gelatin, isinglass does not swell much in cold water. On immersion in water it becomes opaque, but does not gelatinise. This is quite a useful method for detecting adulteration in isinglass.

(3) **Casein.**—Ordinary cows' milk is fundamentally an unstable colloidal solution of casein and fats (butter) in an aqueous serum which contains milk sugar (lactose) in solution. The casein is present in the form of caseinate of lime, which is dispersed in the milk.

The casein is usually manufactured from whey, which is the residue

left after the milk has been used for butter making. Efficient centrifuging in the butter process is essential; this not only increases the yield of butter, but enables the eventual isolation from the whey of a casein with as low a content of fatty matter as possible, the presence of fat being always detrimental in casein that is to be used for adhesives purposes.

The soya bean is also a source of casein, but the market so far is still dominated by milk casein, and as the writer, moreover, has had no experience in the use of soya bean casein in adhesives, this brief reference must suffice.

The best industrial caseins are made by acid precipitation of the whey. This precipitation can be effected by the addition of hydrochloric, sulphuric, acetic or other acids or by the lactic acid which is formed naturally in the curdling process. The curd produced is dried in a centrifuge and washed until the wash waters are quite free from acidity. Since casein rapidly alters and becomes insoluble on subjection to high temperatures, it is dried on shelves in vacuum stoves, or better still, in revolving drums also under vacuum, the temperature not being allowed to exceed 35°-40° C. The product finally is ground and " bolted."

Canada, Argentina, India and New Zealand are at present the largest producers of casein, although efforts which are meeting with various degrees of success are being made to increase its output in the U.S.A. and in the various European countries by the growth of co-operative schemes whereby the whey from numerous producers is worked up for casein at central factories. In any event, from the writer's experience, the user of casein can rely upon getting regular deliveries of good quality non-adulterated material from numerous sources.

Casein is marketed as a white or slightly cream-coloured powder. Too deep a colour is an almost certain indication of inferior quality. Sometimes a dark colour is masked by the addition of a tinting agent, but a rapid test will usually reveal if this has been done. The casein is simply shaken up with water, when the colour of the supernatant solution, after settling, will soon show whether any water-soluble masking dyestuff has been added. The odour of the casein should not be too pronounced, for this is evidence that a certain amount of fermentative decomposition has set in. The moisture content of a casein for use as an adhesive should not be more than 10 to 12 per cent. if the material is to be stable on storage for reasonable periods. This can be tested by drying ten grammes of the casein in an oven at 100°-110° C. to constant weight. The loss in weight expressed as a percentage of the original weight of the casein is the moisture content.

As mentioned above, the most serious drawback to casein for adhesives purposes is the presence of fatty matter, which has a very adverse effect on the tensile strength of the joints made. The method for the determination of fat in a casein is rather too complicated to describe here, but fortunately most of the commercial caseins on the market to-day are quite satisfactory in this respect.

An ash content of more than 5 per cent. is indicative of the adulteration of a casein by the addition of lime, china clay, barytes or the like. The ash content can be determined simply by calcining a small weighed sample of the casein in a quartz crucible.

Acidity in a casein is easily tested for by shaking a few grammes of the material with water; the solution obtained should not redden neutral litmus paper. Free acid in the casein reduces the strength of the joints made. As the acid content increases, the solubility properties of the casein suffer; this means that a greater quantity of water must be used to make the adhesive, with an inevitable increased tendency of the paste to lumpiness.

The finer the degree of subdivision of the casein the more rapid is its speed of solution. In practice, caseins passing sieves of 90/100/110 mesh are used.

Casein is insoluble in water alone but it becomes soluble in the presence of a base, this being the principle of the manufacture of casein adhesives. Borax, as will be discussed later in more detail, is the preferred base since it also functions as an antiseptic, very necessary in such easily putrescible solutions as those of casein. A solution made by dissolving 8 parts by weight of borax in 300 parts by weight of tepid water and then mixing in 50 parts by weight of casein is very homogeneous and clear.

Is is strongly recommended that fresh casein be employed and that the material be stored protected from moisture and air, influences both tending to occasion fermentation in the casein. It is also recommended that the adhesives maker use the untreated casein and not the solubilised product, the base in which has been added to the casein in the course of its manufacture. The drawback to the use of the solubilised caseins is that one can never be perfectly sure as to the nature and quantity of the base that has been added.

The manufacture of a good casein glue, as will be shown later, does not present any difficulties. The principal outlet for the glues is in the wood industry (plywood, veneers, etc.). These casein products are stronger, more waterproof and more resistant to heat than gelatin adhesives, whilst the fact that they do not gelatinise makes them much easier to handle.

(4) **Albumin.**—The purest form of albumin is the dried white of egg. This is the material used largely in the repair of porcelain. The great bulk of industrial albumin, however, is blood albumin produced in large quantities in the abattoirs. The fresh blood coagulates very rapidly. It is stirred with a wicker broom; the fibrin coagulates and the liquid serum is dried in vacuum ovens at low temperatures.

Raw Materials of Vegetable Origin.

(5) **Water-soluble Gums.**—These are adhesive materials derived from the exudations of various kinds of acacias. They can be classified, broadly, into three main groups, in accordance with the nature of the material which predominates in their composition. These materials are arabin (arabic acid), cerasin and bassorin.

The first group, that in which *arabin* predominates, comprises the well-known products gum arabic, gum senegal, etc. The second group, the gums of which are mixtures of arabin and *cerasin*, includes the varieties obtained from fruit trees, mainly from the cherry tree, the plum tree, the peach tree, etc.

Gums in the third group are composed mainly of *bassorin*. They are not so water-soluble as the gums in the first two groups and have very marked swelling properties in water, producing mucilages of more or less pronounced thickness. Gum tragacanth and gum bassora are the principal members of this group. Gum tragacanth is used mainly for sizes and finishes, and also for the preparation of hair fixatives.

For ordinary adhesives purposes the true gum arabics are of the most importance. Gum arabic is soluble in cold water; a simple solution in twice to three times its weight of water is an excellent adhesive which is very stable. Such a solution is mainly used for the sticking of paper. It is not suitable for the production of joints which are expected to resist any great mechanical stress, because the dried film of gum arabic is too crystalline, with a tendency to rub to powder.

Gum arabic is probably on quality grounds the ideal product for the office paste type of adhesive, but its cost is against it, although recent years have seen a progressive reduction in its selling price. For the bulk manufacture of office pastes at competitive prices the starch adhesives to be described later in this book are to be recommended. Modified adhesives can be made which are actually stronger, particularly to degluing, than gum arabic pastes for office work.

(6) **Water-insoluble Resins.**—Reference will be made only to the materials actually used in the adhesives industry. These products are used only in the type of adhesive solution containing organic solvents, with the exception of ordinary rosin (colophony) which can, after saponification, be employed in wholly aqueous adhesive solution.

There are three principal reasons for the use of these gum resins in adhesives. In general, they are cheaper than the principal raw material employed in any particular adhesive. For instance, they are considerably cheaper than latex, cellulose esters, synthetic resins, etc. In the second place, the amount of solid matter in an adhesive solution can be increased by the addition of these gum resins without anything approaching a proportionate increase in the viscosity of the solution. This is a definite advantage with products such as latex and cellulose nitrate, which give highly viscous solutions at relatively low concentrations, the addition of the gum resins in such cases allowing of the production of solutions which leave a denser film and one possessing a lower shrinkage. Without the employment of gum resins this last-mentioned type of adhesive solution, if required to leave similar films, would have to be used at a very high viscosity. In the third place, when used with latex or cellulose adhesives, the gum resins increase not only the hardness and lustre of the films but also, and to a very marked degree, their adhesive power.

To the adhesives maker rosin itself is the most interesting of the gum resins. It is very cheap and very abundant. The United States are the world's largest producer, but closely followed by France, Spain, Portugal and Russia, whilst the importance of the Indian industry is increasing. Rosin or colophony is the resinous constituent of the oleo-resin exuded by various species of pine. The separation of the oleo-resin into turpentine and common rosin is effected by distillation in large stills.

Rosin varies in colour, according to the age of the tree whence the oleo-resin is drawn and the amount of heat applied in distillation, from an opaque almost pitchy black substance through grades of brown and yellow to an almost perfectly transparent colourless mass. The commercial grades are numerous, ranging by designating letters from "A," the darkest, through "N," extra pale-superior, to "W" "window-glass" and "WW" (water-white) varieties, the last-mentioned grade having about three times the value of the common qualities.

The French rosins contain less turpentine and are generally paler than the American rosins owing to the fact that steam distillation is usually adopted in the Landes district for the treatment of the oleo-

resin, whilst in the United States open-fire distillation is still extensively employed.

As rosin itself is rather soft and friable, it is sometimes given a hardening treatment by heating with hydrated lime or zinc oxide. Heating rosin with 6 per cent. of its weight of hydrated lime or with from 2 to 4 per cent. of its weight of zinc oxide gives a material which melts at about 50° C. higher than the original rosin.

A much superior form of modified rosin is the well-known "ester gum," made by the treatment of rosin with glycerin. This is discussed in more detail in the section on synthetic resins.

Rosin is soluble in practically all the organic solvents, and finds employment in numerous adhesives of the water-immiscible type, where it functions mainly, though not entirely, as a cheapening agent. It can be employed in aqueous adhesives after conversion to water-soluble alkali resinate by treatment with a suitable alkali. This alkali resinate, or "rosin size," is used mainly in the paper manufacturing industry but, as will be seen later, is not without interest in the usual type of adhesive.

The other gum resins, such as copal, mastic, kauri, dammar, elemi, congo, etc., are in general too expensive to warrant their use in adhesives. They find their main field of application in the production of varnishes.

(7) **The Gum Elastics.**—Natural rubber is derived from the milky fluid (latex) which exudes when incisions are made into the cambium layers of a number of trees and shrubs of tropical habit. The *Hevea braziliensis*, which grows wild in the forests of Brazil, and which is the tree cultivated practically exclusively in the rubber plantations of Malaya and Ceylon, yields the best type of natural rubber. In the early days of the rubber industry the smoking process was used for the coagulation of the natural latex, but on the plantations to-day the latex is mainly coagulated by the addition of acids, principally acetic acid, although formic acid is making distinct headway. After coagulation and washing, the rubber is marketed in the form of pale crêpe or as smoked sheet, the former being the superior quality and the one most suitable for the preparation of adhesive solutions.

Processes are being developed whereby the rubber is produced in powder and softened forms. This is of interest to the adhesives maker owing to the greater ease with which powder or "crumb rubber," owing to its greater surface per unit of weight, will go into solution. These developments need only be merely mentioned here, as the literature of the rubber industry is adequately extensive. At the moment, the adhesives maker is mainly interested in pale crêpe and smoked sheet and, to a growing extent, in rubber latex itself. The

opening-up within the past decade or so of direct uses for latex has been accompanied by increased shipment from the plantations of the rubber latex itself, usually concentrated and stabilised against decomposition during transport and storage.

Rubber latex is an extremely dispersed emulsion of rubber globules in a medium which consists of an aqueous serum containing proteins, sugars, a lipase, fatty acids, mineral salts and resins. As a suspensoid system, latex offers many points of similarity to ordinary cows' milk. Like the latter it is extremely susceptible to bacterial fermentation, the acid products formed by bacterial action leading to the separation of the rubber as in the analogous case of the separation of casein from whey. This coagulation of the latex is prevented by the addition of 12 to 20 c.c. of 28 per cent. ammonia per litre of latex, followed by filtration, concentration, etc. Other materials such as formaldehyde, etc., are also used to prevent either the coagulation of the rubber or the tendency to cream which is shown by the more concentrated latices.

The ammonia assures the maintenance of alkaline conditions in the latex. It has the further advantage that it forms ammonium compounds with the fatty acids and some of the resinous products in the latex, these latter compounds then functioning as stabilising colloids in the suspension. For the small-scale user, latex is usually sold to-day in eight-gallon cases and in concentrations (in terms of actual rubber content) of from 35 to 75 per cent.

Gutta-percha is a material somewhat allied to rubber, with the exception that it is plastic and not elastic. Its price is against it for adhesives work, for which it offers no marked advantages over solutions of rubber with other incorporants.

(8) **The Algæ.**—The algæ or seaweeds are also capable of producing solutions of some interest to the adhesives industry. Strictly speaking, the products obtained from the algæ are not true adhesives, but mucilages of the gum tragacanth type, which possess great thickening power and are consequently capable of taking up a considerable weight of water. These mucilages can be employed for thickening true adhesives of the starch, casein, etc., types.

The seaweed is washed carefully with soft acidulated water and then heated with a solution of sodium carbonate to produce the sodium alginates which are the actual mucilaginous product. The alginates of sodium and magnesium are soluble in water; those of most other metals are insoluble.

(9) **The Starches and Flours.**—We now come to the most important and interesting group of raw materials for the production of cold adhesives. Starch, especially potato starch, and more especially still

cassava starch, is susceptible of undergoing the most varied range of changes and is capable of producing adhesive solutions wholly or substantially equivalent in properties to solutions made from the most divergent types of raw materials, such as rubber, the cellulose esters, etc. The field for investigation presented by starch-derived adhesives even to-day offers numerous opportunities.

Although in chemical composition and properties the two groups of materials are substantially identical, the designation "flour" is usually reserved for amylaceous substances derived from cereals, and the designation "starch" for similar materials extracted from tubers or roots such as the potato, cassava, etc.

The exact chemical composition of the flours and starches is as complicated as it is controversial. For our strictly utilitarian purposes, however, it may be considered that the granules of these materials are composed of amylose, which is the soluble portion or the true starch, and amylo-cellulose, which is a more resistant material of affinities allied to lignin. The term "amylo-cellulose" is adopted by the author in preference to "amylo-dextrin" because in certain of the modification treatments to which the starches can be subjected it seems to behave more like a cellulosic material than a dextrin.

Under the microscope, the potato starch granules reveal an elliptical shape, with a hilum at one point surrounded by concentric channels or grooves. The cassava starch grains are smaller, fairly regular and more angular, and they have an unmistakable eccentric stratification.

The working-up of the starch consists in principle in separation of the amylaceous granules from the pulpy material by which they are surrounded. The potatoes are first carefully freed from their adhering mud by treatment in rotary or screw washing machines. The washed tubers are conveyed to rasping machines, where they are disintegrated under the influence of a continuous jet of water into a very fine pulp, the object of this treatment being to liberate the individual starch granules. The coarse "solution" so obtained is given a preliminary sieving to separate the pulp, the starch granules passing through the meshes of the sieve used. Rotary sieves with mechanical cleaning brushes are used to prevent the rapid blocking-up of the meshes which would otherwise occur.

After this first purification, the starch is separated from the washing liquor by settling in stagnant water in the decantation vats, or in running water by making the starch suspension traverse long and narrow channels termed settling channels. Use is also made of separating and purifying vats (the Uhland method) in which the principle is adopted of gradually decreasing the speed of the circulating

starch suspension, whereby the heavier starch granules settle at the bottom of the V-shaped channels, the lighter fibrous material being maintained in suspension by the water.

The starch separated by any of the methods outlined above still contains about 50 per cent. of water and is freed from most of this by passage through a centrifuge. Drying is then completed in an oven or tunnel drier, the most modern and best method being a cylindrical vacuum drier in which the temperature can be kept low enough to avoid the formation of a pasty mass.

In its general outlines, the working-up of cassava starch is similar to that of potato starch, but certain additional precautions have to be taken. The purity of the water used is important enough in the potato starch industry, but when cassava starch is being made, the question of water supplies assumes paramount importance. Cassava always contains a little tannin, and if there is any iron in the water, even traces, tannate of iron will be formed. This tannate diffuses into the starch, cannot be removed by washing, and results in the production of a cassava starch of a distinctly grey colour. It was this difficulty which led to the failure of an important cassava starch manufacturing venture in the North of France. For the same reason the use of iron in the construction of plant for the industry is to be ruled out. Wherever the metal is likely to come into contact with the starch, copper or aluminium should be used.

Cassava starch is produced in France from imported dried cossettes. These cossettes are ground and the starch then soaked out with water. This procedure gives more satisfactory results than that adopted in the case of potato starch, since it is easier to control the purity of the water used. The steeping vats employed are glass-lined, lined with ceramic tiles with joints of paraffin wax, or are coated with magnesium fluosilicate.

When working with dried cossettes it is not possible to obtain cassava starch of quite as fine a quality as when fresh cossettes are used. This is easily understandable, since during the transport of the material the complete exclusion of extraneous matter cannot be wholly secured, whilst decomposition, which might only be very slight, occurs and is reflected in the quality of the extracted starch.

The French cassava starch industry uses Madagascan cossettes as its principal raw material. Preference is given to cassava harvested on the high plateaux, as this is richer and less fibrous than material grown in the coastal districts. It is the general practice to treat the cossettes in the steeping bath with a small quantity of sulphur dioxide, which decolorises certain pigmentary materials and helps in the production of a whiter starch.

It must be admitted, though, that as in the case of potato starch, Dutch cassava starch is in general superior to the French product.

The Dutch starch factories have a long experience behind them, and their plants as a rule are more efficient and up-to-date. Further, much of the Dutch cassava starch is made on the spot, in the Netherlands Indies, the freshness of the raw material in this case being a further and substantial advantage. As a user of rather large quantities of Dutch cassava starch, the writer willingly bears testimony to the quality and perfect uniformity of certain well-known brands.

Cassava starch is made by two firms in France. One makes a product which is white enough, but which is rather pasty; the other makes a starch which is not quite so white, but which gives more viscous solutions. The latter type is the one which has been found the better for adhesives making. A third French firm is reported as having decided to produce cassava starch in Madagascar, and if this project materialises the user should have another product of a quality equal to that of the Dutch material.

Potato starch and cassava starch are both raw materials for the production of vegetable adhesives and of dextrins. The writer's experience has shown, however, that other things being equal, the preference always lies with cassava starch, for the following six principal reasons:

(1) Cassava starch is cheaper.
(2) It possesses a higher gelatinising power.
(3) It gives more viscous pastes.
(4) It gives much more stable pastes than does potato starch, the last-mentioned frequently showing a tendency to revert.
(5) It can be solubilised more easily and thus enables more convenient production of concentrated soluble starch pastes.
(6) The pastes obtained by its use have not the disagreeable odour possessed by potato starch pastes.

The quality of a sample of starch for commercial purposes is judged roughly by testing its fineness, freedom from grittiness to the touch, and by examining its whiteness against the background of a sheet of blue paper. A more reliable, yet still simple, test consists in putting a few grammes of the starch into a porcelain dish and adding a little petroleum spirit. According to its greater or lesser degree of purity, the starch will acquire a more or less pronounced grey tint. By gently swirling the contents of the dish the impurities can be isolated as a separate deposit.

The final and irrefutable arbiter of the suitability of a starch for adhesives making lies, of course, in making up samples of paste with

equal weights of the starch samples under comparison. Five grammes of the starch are heated for four minutes on the boiling water-bath with 60 grammes of water and the various pastes tested by the methods described in the last chapter. Strictly comparative conditions should be observed, of course, in these trials: the time of heating should be exactly four minutes; the pastes should be stirred carefully with a glass rod, particularly at the beginning of the heating, to assure the production of a uniform paste free from lumps which, if present, will vitiate the results; on removal from the water-bath the dishes should be covered with watch glasses and allowed to stand for at least 12 hours before comparing the pastes for colour and viscosity.

No matter whether potato starch or cassava starch be used, preference should be given to those products giving viscous pastes rather than doughy pastes, for whilst it is simple to make a doughy paste from a viscous paste, the reverse operation is far from easy.

(10) **The Dextrins.**—The dextrins come second in importance among the raw materials of the maker of cold adhesives. Their consumption is steadily increasing, not only for adhesives manufacture but for other purposes. In one sense the dextrins can be considered as substitutes for the natural water-soluble gums. The dextrins are cheaper than these gums, but they are almost equally water-soluble. They also possess less pronounced thickening properties, and so allow of the production of more concentrated solutions, which are very sticky and rapid-drying.

Dextrin is a product of the transformation of the flours or starches, the changes which these materials undergo on hydrolytic decomposition being represented very simply as

Starch→Soluble starch→Dextrin→Glucose

The transformation is usually effected by one of the three following methods: By roasting the starch at high temperature; by the intervention of a diastase; or by the action of hot dilute acids. The first and last-mentioned methods are by far the most important and are the only ones which can be described here.

The problem to be solved is to transform the starch into dextrin and obtain a final product with the highest viscosity and least colour possible and with the minimum content of glucose. Glucose diminishes the adhesive value of a dextrin and introduces unwanted hygroscopicity. The danger of its formation is largely obviated by treating the starch in the presence of the lowest possible quantity of moisture, since the presence of water is favourable to the formation of glucose. Another important point is to make sure that the mixture of starch and acid is as uniform as possible. For this reason, mineral

acids capable of partial or total volatilisation are preferred, since such volatilisation ensures regularity of diffusion of the acid throughout the mass being treated. For this reason again, processes which use not a dilute solution of the acid but the acid gas are also in use.

The industrial production of the dextrins comprises the following stages: Acidulation, drying, roasting, cooling, moistening and "bolting." The nature of the plant used depends upon the scale of the output, but for small-scale work the plant can be considerably simplified and the process can even, as will be seen later, be carried out in a single pan.

(*a*). *Acidulation.*—The weighed charge of the starch is put into the reaction vessel, where it is stirred up energetically by a suitable agitator. The dilute acid is added and intimately mixed with the starch mass by a blast of compressed air. By the dual action of the stirrer and the compressed air, perfectly homogeneous impregnation is secured.

(*b*) *Drying.*—The concentration and quantity of the acid should have been so chosen that the acidulated starch contains from 23 to 25 per cent. of water. Most of this water must be removed before the roasting to minimise the formation of glucose. This is effected by vacuum drying, which reduces the water content of the material to 2 to 3 per cent. The drier consists of a horizontal cylindrical vessel provided with a double steam-jacket and fitted internally with rotating arms to which shovel-type blades are attached. These blades continuously mix and stir the material that is being dried. As the apparatus functions under vacuum, there is no danger of the starch being overheated, despite the fact that it comes into direct contact with the hot inner surface of the drier. The vapours escaping pass from the moisture dome to a dry diffuser which separates the greater part of the granules entrained towards the end of the process, the rest being entrapped in a wet diffuser. The vapours finally reach a surface condenser or, more simply, an injection condenser directly connected to the air-pump, where they are precipitated by the cooling.

(*c*) *Roasting.*—The acidulated, dried starch is transferred to the roasters, which are horizontal flat vats fitted with stirring paddles mounted on a vertical shaft. Heating is effected by direct fire, hot air or, best, by superheated steam passing through the jacket of the roaster. Depending upon the nature of the acid, its percentage and the temperature and duration of the roasting, any one of the range of dextrins (white, yellow or deep yellow) can be obtained.

(*d*) *Cooling.*—When the desired degree of dextrinisation of the starch has been obtained, the material must be cooled to stop the reaction.

(*e*) *Moistening.*—The cooled material is in a practically anhydrous condition and water has again to be added. This is not only to bring the material to accepted commercial strengths, but also to improve its solubility properties, since anhydrous dextrin does not dissolve very easily and has a tendency to form lumps.

The hydration can also be effected simply by exposing the dextrin to the atmosphere, but this is a lengthy process and one which cannot be relied upon to produce a homogeneous material. On the industrial scale, use is made of a humidifier consisting of a wooden silo, together with an elevator for the dextrin and a distributing arrangement with the necessary blowing machinery. The principle consists in blowing a current of air mixed with steam in counter-flow to a descending stream of the finely-divided dextrin.

(*f*) "*Bolting.*"—In this final process the dextrin is passed through a vibrating sieve which removes impurities and retains outsize particles, the commercial product being a finely-divided uniform powder.

Owing to the difficulty of exactly duplicating two successive batches, the larger makers employ plant of large capacity or secure standard products by the judicious mixing, after testing, of various batches.

For the needs of the small maker the process outlined above can be simplified in various ways. If the dextrin is to be used in the same works, the steps of cooling, hydrating and " bolting " can often be omitted, whilst with some modifications the various operations of acidulation, roasting and drying can be carried out in one and the same vacuum drier.

Still more simply, for very small productions, the process can be conducted in a single mixer. This mixer consists of a vat jacketed both on its sides and bottom and fitted internally with a helicoidal agitator which assures perfect scraping and mixing of the charge in both the horizontal and vertical directions. The vat should be capable of being heated with steam at 10 atmospheres pressure.

Working with such a simplified plant, part of the starch is mixed with the acid solution to produce a thick broth which is transferred to the vat and well mixed. Heating should be fairly gentle at first since the main immediate object is to secure the evaporation of the excess moisture. Commencement of dextrinisation under these conditions cannot be avoided, however, nor can the production of some glucose under the moist conditions obtaining. When the bulk of the water has gone, the temperature is raised and roasting conditions reached, the dextrin being withdrawn from the vat when the conversion has gone far enough.

The selection of a dextrin for adhesives making is not a simple matter. There are no generally accepted commercial standards

and the products available differ markedly in viscosity, colour, adhesive power, etc. This is readily intelligible when it is remembered that the dextrinisation process can be stopped at any one of thousands of stages between the initial soluble starch and the final glucose.

The only test of real value is to subject samples of dextrin to comparative trials as in the case of the starches, a suitable solution for test purposes being made up by dissolving 30 grammes of dextrin in 21 grammes of water on the water-bath for three minutes.

Even those commercial dextrins which have been the most completely converted contain a certain proportion of incompletely modified starch, which goes into solution only on the application of heat. That is why the water-bath should be used in making up the test solution.

Little attention need be paid to the white dextrins, which are the insufficiently modified products and which are characterised by a greater thickening power than the more thoroughly converted materials. To prepare adhesive pastes from the white dextrins weights of water from two to three times that of the dextrin are needed, but pastes of this concentration, as will be shown later, can be made just as well from other raw materials.

In the examination of dextrin sample pastes made as described above, the following points should be borne in mind : The paste should be allowed to stand for at least 24 hours before subjecting it to any test. Colloidal solutions of adhesive materials which are only partially soluble or insoluble in cold water tend to revert and to set into a block, this tendency being the more pronounced the stronger the solution and the lower the temperature at which it is stored.

In the case of a dextrin, there is always a cold-water insoluble portion, greater in the white dextrins and less in the more transformed materials. As a consequence, the soluble portion functions as a suspending agent for the insoluble portion ; the higher the percentage of the soluble portion the more stable the equilibrium of the suspension, whilst the higher the percentage of the insoluble portion the more will it exert its influence towards thickening the solution and towards the eventual production of a solid block. This is why it is advisable not only to wait at least 24 hours before carrying out the preliminary tests on a sample of dextrin paste, but to keep the paste for about a month before subjecting it to the final tests. During this month the paste should be kept in a cool place to give any trends to reversion opportunity to reveal themselves.

As an example of these testing methods, let us assume that we are wishing to make a very dense and consequently very rapid-setting

dextrin adhesive containing the minimum of water, and that two different samples of dextrin have been offered us for the purpose. After 24 hours dextrin " A," the less transformed material, gives a more viscous and more adhesive solution than does dextrin " B," which is almost completely soluble and which gives immediately a very fluid solution. If now, a fortnight later, we re-examine these samples, which have been preserved in a cool place, we find that dextrin " A," which seemed so good on the first test, has completely hardened and set into a block, whilst dextrin " B " has retained a good viscosity and shows itself as really the better of the two for the purpose required. If on the other hand we are wanting to make a dextrin paste of medium concentration and one in which we intend to ensure the stability and augment the viscosity by treatment with alkalis, which act mainly upon the soluble starch content, then dextrin " A " presents advantages.

In the interests of both makers and users of dextrins some measure of standardisation in the trade seems advisable. The reluctance of makers to take steps in this direction is probably due to the demand from individual users for special grades of the material. But, after all, two grades of dextrins are all that is really needed ; one which is highly dextrinised and almost completely soluble, and so possessing the maximum of adhesive power, and a second which is less transformed. Whatever be the type of dextrin adhesive to be made, a suitable raw material can be provided by the judicious blending of two such standard grades of dextrin.

A test that it is always advisable to carry out, particularly with very soluble dextrins, is to spread the solution on a sheet of glass and to store the sheet in a humid place. Any pronounced degree of hygroscopicity due to an unusually large amount of glucose will soon show itself. Within reason, of course, a certain degree of hygroscopicity is an advantage in a dextrin, particularly when highly concentrated solutions are to be made. In fact, when the dextrin seems unusually free from hygroscopicity and very strong pastes are to be made, it is of advantage even to add a little hygroscopic agent to give the dried film a certain degree of plasticity.

The whole question of the dextrins and their manufacture is a complicated one. In the writer's opinion the whole basis upon which their manufacture rests is wrong. This question will be returned to later, when an original process will be described which allows of the simple production of pale uniform dextrins which are perfectly soluble, very sticky, and at the same time free from glucose. In this process there is no apparent morphological transformation in the starch granules.

(11) **Sucrate of Lime.**—A solution possessing a sticky and pseudo-adhesive nature can be obtained by heating an aqueous solution of freshly hydrated lime with cane sugar or beet sugar. By itself this solution is of but minor technical interest but, as will be shown later, it is often used for the preparation of cold gelatin-type adhesives.

(12) **Sulphite Cellulose Lye.**—The process most widely adopted nowadays for the production from wood of pulp suitable for the manufacture of paper or of artificial silk of the viscose type is that dependent upon the treatment of the wood with solutions of bisulphites. The waste liquor resulting from this process, which contains in solution and in suspension the numerous tannin, lignin, mineral and colouring constituents of the original pine wood chippings, is known, after subjection to a certain degree of decolorisation, purification and concentration, as " waste sulphite lye or liquor." This waste product is produced in very great amounts and research has long been directed to the problem of finding new and increased uses for it. The adhesives industry has naturally attracted attention as a possible outlet, but it cannot be claimed that the results so far achieved have been particularly striking. Used alone, waste sulphite lye is not a practicable adhesive, but numerous attempts have been made to reduce its hygroscopicity by additions such as lime, and to improve its adhesive powers by the incorporation of gelatin, casein, etc. In the writer's opinion, which he admits is a purely practical and commercial one, time spent in the attempt to utilise waste sulphite lye as an adhesive might more profitably be spent in other activities, since equivalent adhesive materials can be made from starches at no greater cost than from sulphite lye, even taking the lowest probable market value for the latter as the basis for comparison.

(13) **The Synthetic Resins.**—The chemical synthetic products falling within this group nowadays constitute a very important and varied group of materials. Their original development was to some extent accidental, but the early work on the products of the phenol-formaldehyde class soon revealed their probable importance both as substitutes for the natural gums and in opening-up entirely new fields of application. Some of these products are of undoubted interest to the maker of adhesives, and as experience in their employment grows, there is no doubt that they will prove progressively more important as constituents of adhesives, not only for such special purposes as the manufacture of laminated safety-glass products, but also for more general work. Their great advantage is that they produce by simple solution in a suitable solvent or mixture of solvents a material which is colourless and viscous and which leaves on drying a hard and tough yet flexible and firmly attached film.

A very large number of synthetic resins is already on the market and their range grows continuously. Some of the materials are sold under trade names which offer no clue to their real nature, but the majority of the products are no secret as regards their chemical composition. Leaving out of consideration synthetic rubber which could, one supposes, most logically be grouped among the synthetic resins but which, in any case, is not yet a commercial proposition, the synthetic resins may be classified into the following main groups: (i) The coumarone resins, (ii) the resins from acetylene, (iii) phenol-aldehyde resins, (iv) urea and thiourea-formaldehyde resins, (v) the amine-formaldehyde resins, (vi) the "alkyd" resins, (vii) the vinyl resins, (viii) the ester gums (glycerin rosins), and (ix) the accroleids, or products of the interaction of phenol and glycerin.

The ester gums and the coumarone resins are the cheapest among those listed. Used alone they do not give satisfactory adhesive solutions since their solutions are lacking in viscosity and yield films which are deficient as to hardness, resistance and flexibility. They are both exceedingly valuable materials, however, as additives to adhesive solutions made from cellulose nitrate, cellulose acetate or rubber, whilst they can further be advantageously employed to reinforce the adhesive action of solutions of other synthetic resins.

The coumarone resins are produced from coal-tar naphtha fractions boiling at 150°-200° C. These fractions in solution in benzene are acted upon by sulphuric acid, resinous substances being formed by the polymerisation-condensation of the coumarone contained in the naphtha. An alternative procedure is to heat the naphtha with small quantities of concentrated sulphuric acid or with aluminium chloride. Coumarone resin is not saponifiable with soda, and cannot therefore be used in the manufacture of aqueous adhesives as can rosin. From the viewpoint of the adhesives maker the great advantages of coumarone resins are their neutrality, resistance to both acids and bases, and absolute impermeability to water.

Coumarone resins and ester gums are largely competitive materials, the prices for ordinary grades being about equal. Ester gum is perhaps the most widely used rosin ester. It is prepared from common rosin and glycerin, 10 to 15 per cent. of the latter being heated with the rosin after the rosin itself has been heated to 350° C. *in vacuo* to remove volatile constituents. The treatment with the glycerin is effected at 250° C., sometimes at ordinary pressures but, for the best products, under a pressure of several atmospheres. When the esterification is as complete as possible, the ester is distilled to separate the hard and soft portions.

Zinc oxide or lime is sometimes added to accelerate the process,

but usually at the expense of the colour of the material produced. The process is generally conducted in an aluminium pan provided with a reflux condenser which allows the water liberated in the reaction to escape, but which condenses and returns any glycerin vapours. The acid number of a normal ester gum is from 6 to 8 as compared with an acid number of about 200 possessed by the original rosin. The melting-point and the hardness of the rosin are raised by the conversion. Ester gum is marketed in pale and super-pale grades. Although in outline its manufacture is fairly simple, in practice difficulties do arise, and regular and high-grade supplies being available on the market, the production of ester gum is not an operation upon which the adhesives maker can be recommended to embark lightly.

The resins of the phenol-aldehyde type are probably still those in widest use to-day. They are often termed "bakelites," after Dr. Baekeland who, in 1909, first made their production a commercial possibility. They are manufactured by condensing phenol or cresol with formaldehyde, paraformaldehyde or hexamethylene tetramine. To go into any great detail on the subject would be impracticable here, and in any case the literature on the subject is already voluminous. It may be pointed out, though, that the condensation reaction passes through three main stages. The first is the production of an initial resin ("*a*") which is soluble in the usual organic solvents, particularly in methyl and ethyl alcohols. The resin "*b*" formed in the second or intermediate stage is produced on further heating. It is harder than resin "*a*" and is insoluble. It can be softened by heat to a rubber-like consistency, but cannot be fused. The final stage, or "*c*" resin, is reached after prolonged heating. The resin is now completely insoluble, can be heated to 300° C. without softening, and is resistant to the action of oils and boiling dilute solutions of acids and alkalis. These materials find their main use in moulded plastics, but they also possess interest as adhesives, the resin being applied in the "*a*" condition and then converted into the "*c*" condition. The joints produced are practically indestructible, but they are brittle and inflexible. By heating the phenol-formaldehyde resins with rosin the Albertol and Amberol modifications are produced. These substances are excellent substitutes for natural copal in varnishes.

The urea-aldehyde and "alkyd" (glycerin-phthalic anhydride condensation products) resins are now widely used materials, the former in the moulding and the latter in the varnish industries. By effecting the condensation of urea and formaldehyde in the presence of zinc chloride, an American firm has recently produced a material claimed to be particularly suitable as a base for plywood and veneer adhesives.

The amine-formaldehyde resins are produced by heating aniline

or other amine with formaldehyde for some hours at 130° to 140° C. in the presence of an acid. They have already found certain specialised applications in adhesives work, particularly in the production of laminated paper for electrical insulation work. As to the applicability for general adhesives, experience is still lacking.

One of the most interesting types of synthetic resin for the adhesives maker is that termed the vinyl resins. These products are made from vinyl esters, for instance vinyl acetate, produced by passing acetylene gas rapidly through acetic acid in the presence of mercuric sulphate as a catalyst at a temperature of about 70° C. Other vinyl esters are made similarly, using the corresponding acids. Polymerisation of these esters is brought about by the action of heat and light, with the production of solid, transparent, water-white resins. They are soluble in a wide range of organic solvents, are widely used in the safety glass industry, and their use as general adhesives is discussed later in this book.

(14) **Cellulose.**—Of the various cellulose derivatives it is the nitrate which at the moment possesses most interest to the adhesives maker. The acetate is, of course, also a well-known product in the form of artificial silk, etc., but generally for ordinary adhesives work its price is against it as compared with the nitrate. Little information has been published on the use of cellulose acetate in ordinary adhesives, but the makers are understood to have investigated its possibilities and, in some instances, are prepared to give technical advice to prospective users.

The cellulose nitrate used by the adhesives maker is the well-known nitro-cotton of the cellulose lacquer and the celluloid industries. It is made by the treatment of cotton, usually purified bleached cotton linters, with a mixture of nitric and sulphuric acids. As the product, although not as highly nitrated as guncotton, is still highly inflammable and explosive, it is not dried after making, but the water content of the material is displaced by alcohol. The adhesives maker, however, finds waste celluloid cinema film from which the photographic layer has been removed, but which still retains most of the camphor used as plasticiser, his most suitable raw material on both price and quality grounds. The great advance in the manufacture of nitro-cotton for industrial purposes during recent years has been in the production of materials which give in organic solvents solutions of reduced viscosity by exact control of the reacting quantities of materials and the conditions during the nitration process. Commercially, nitro-cottons are sold on the basis both of their nitrogen content and their description "in seconds." The last-mentioned is a measure of the time taken in seconds for a

steel ball to fall through a glass tube containing a solution of the cellulose nitrate, the exact conditions of the test being fixed by international agreement. The shorter the time of fall of the ball the lower naturally is the viscosity of the solution.

Raw Materials of Mineral Origin.

(15) **Sodium silicate** is the only product which in practice falls within this group. Its preparation and properties are described in the separate chapter on the subject.

CHAPTER V.

MANUFACTURING EQUIPMENT.

MANUFACTURING methods for cold adhesives can most conveniently be discussed under two headings, namely manufacture on the small scale and manufacture on the large scale.

The Small-scale Production Methods.—The starch-derived adhesives offer the most difficulties to the maker of small batches. The production of starch pastes by the wholly cold processes, in which concentrated solutions are treated with a base or a salt, is quite impracticable without the help of mechanical stirrers. The extremely tenacious and viscous paste formed at the very commencement of this process is practically impossible to stir by hand. There is a second reason, moreover, why this process cannot be carried out on the very small scale. The quality of the pastes produced depend in very large measure on the efficiency of the mixing, or rather the beating, and to assure adequate beating by hand operation would require an inordinately long time.

With starch adhesives obtained by the hot processes, although the paste becomes more or less fluid at the end of the manufacturing operation, there is an intermediate phase during which the consistency and thickness of the mass are almost as great as in the case of the more concentrated adhesive products. A ratio of water to starch of about eight to one is about the lowest for satisfactory incorporation by hand stirring. A mixture of six parts of water to one of starch is incorporated only with great difficulty.

The heating arrangements for small-scale work need only be very simple. A water-bath can be made simply by selecting two receptacles, one of which fits in the other, the water being placed in the outer receptacle. If boiling water temperatures are inadequate, the water can be replaced by oil, or more economically and just as effectively, by a saturated solution of calcium chloride.

Dextrin adhesives offer no difficulties in small-scale manufacture no matter what their concentration. The dextrins used in making the more concentrated solutions are, in fact, the varieties which are most

soluble in water. The employment of heat in making dextrin adhesives is merely for the purpose of facilitating solution.

Adhesive solutions which consist of materials like synthetic resins and cellulose nitrate in organic solvents can readily be made on the small scale, although care must be taken to avoid risks of fire. The same is true for adhesives obtained by fusion and direct heating, which usually demand only slight mixing. Powdered products can be prepared on the small scale by placing the various constituents in a light container, a galvanised sheet container for instance, which can be tightly closed. If not more than one-fourth of the volume of the container is occupied by the mixture, adequate and thorough incorporation of the constituents can be obtained by vigorous shaking.

Plant for Large-scale Production.—In principle, most mixing machines of the kneading or masticating type are suitable for the production of cold adhesives, the main requirements being substantial construction, since the pastes handled are usually very stiff. In the writer's experience, however, the best type of plant is that in which the shaft is horizontal and the blades are of the double helical Z type.

Unless the plant is to be used for the regular production of one type of adhesive, the use of wooden vats is not advised, for in such cases the only heating method possible is by the injection of steam. Further, it is impossible to avoid impregnation of the wood by materials used, the presence of which, even in small amounts, may prove harmful when the vat is employed for making other types of adhesive.

In a vertical mixer, the mass tends to pile up at the bottom and it is difficult to attain perfect homogeneity, particularly with very stiff pastes. In a horizontal mixer, the mass being treated is continuously being brought to the top, dropped, divided and cut-up by the blades and, in practice, this type of mixer has proved exceptionally satisfactory with very stiff pastes. The advantages possessed by the horizontal mixer also hold good when making solutions in organic solvents. Further, when using a jacketed horizontal mixer for processes demanding the application of heat, local overheating is avoided more positively than with the vertical mixer.

The Horizontal Mixer-kneader.—From the viewpoint of efficiency, the ideal type of plant is the horizontal mixer-kneader fitted with two shafts, each mounted with helical Z-blades. The two shafts rotate in opposite directions, one at double the speed of the other. The blades are so shaped as to whip the contents of the batch being worked from the periphery to the centre of the mixer. A plant of this type is usually constructed of machined cast-iron or, more simply, of riveted and autogenously welded iron plate. Emptying is effected by tipping-up mechanism actuated either by hand or by engaging gear.

The lid is lifted either by a winch or by counter-weights. The drawbacks to this type of plant in practice are twofold, namely, its rather high cost and its mechanical complexities, and for general purposes, in the writer's opinion, there are few cases where a horizontal mixer-kneader with a single shaft mounted with helical Z-blades will not suffice.

The ideal mixer would be of spherical shape, but in practice the usual rectangular form is not a pronounced drawback. The shaft should be capable of rotation at two speeds, of about 10 and 40 revolutions per minute respectively. The exact speeds are dependent, of course, upon the size of the blades, for the larger the diameter of the blades, the higher will be their peripheral speeds for any given speed of rotation of the shaft. Provision for actuation at two speeds involves the installation of a further train of gears, but does not add very much to the cost of the plant. The adoption of two speeds is advisable for the following reasons: (*a*) Operation at low speeds is useful when, at the commencement of certain batches, the mass is very thick, or when too violent agitation, especially when working at high temperatures, is inadvisable. (*b*) Ability to run the shaft at high speeds is useful when small quantities of additional constituents have to be added to a batch, or when any chemical reactions involved in making the adhesive solutions are capable of acceleration by the mechanical factor.

Other things being equal, individual drive by direct-coupled electric motors through gearing of laminated synthetic resin material is advisable. As occasional overloading is always a possibility in this type of process, the horse-power of the motor should preferentially be chosen so as to leave ample reserve power in hand.

The idea of making the mixing vessel of semi-circular cross-section might seem attractive as a means of facilitating the efficiency of the beating operation. In practice, however, such a method of construction is not an advantage, since it reduces the useful volume of the mixer, adds complications to constructional methods and renders cleaning rather more difficult.

The mixer should be fixed solidly in position and erected at a high level, so that on emptying, containers can be filled by gravity fall. The height at which the mixer is to be erected depends, of course, upon individual considerations. Emptying is effected by one or two gate valves, according to the size of the apparatus. These valves should have an orifice diameter of 90/100 mm. and allow of rapid and smooth emptying. Where the mixer is steam-jacketed, a short length of piping naturally penetrates the jacket and as the small portion of the batch which fills this short length of piping is not subject

to the action of the stirring blades, it very often sets solid and forms a block. This can easily be removed before emptying by stopping the agitation and loosening with a rod.

In the author's experience, very thick and viscous products can be run off from gate valves of the size specified, very easily. In those cases where the paste is exceptionally stiff and possesses very little viscosity, arrangements can be made to empty the mixer by rocker action, the single horizontal axis being so arranged that the mixer can be rotated around it. The practicability of this method of emptying is a further point in favour of the single-shaft horizontal mixing plant.

The height of the double jacket for steam heating purposes should preferably be such that the top of the jacket is about two or three centimetres below the point at which the blades most nearly approach the side walls of the mixer. This is to avoid the possibility of the material being overheated by coming into contact with parts of the hot wall which are not subjected to the scraping action of the stirrers. With a steam jacket of this type the heat transfer is more rapid in a single-shaft mixer than in a double-shaft mixer.

Great importance must be attached to the construction of the stuffing box. Preferably this should be made of an oxidation-resistant metal and be long enough to enable thorough packing of the plastic material. The gudgeons should be of large diameter, the threading wide and the screws with large sides. The boxes should be strong enough to stand unblocking by hammer blows without breaking. They should be constructed in two parts, one being the stuffing box proper and the other serving as the rotation bearing. The lid of the mixer should be well fitting. With mixers of above a certain capacity it is preferable to utilise a fixed lid, charging being effected through a manhole.

The interior of the mixer above the stirrer blades, as well as the inner surface of the lid, should be lined with screwed-on sheets of copper or brass. Lead is less suitable in this connection. This additional expense is well repaid by the avoidance of troubles due to rust, particularly when working by the heat processes. Rust discolours, and tends to coagulate, the solutions, particularly with the starch adhesives. Lining the whole interior of the mixer with copper is not essential. All that is really necessary is to protect from oxidation the part of the mixer which is not covered by the solution.

The steam jackets are generally designed to stand pressures of six atmospheres, sufficient for apparatus with a useful capacity of 200 to 250 litres. Mixers of greater capacity are less efficient from the heat exchange viewpoint.

Heating by the direct injection of steam into the mass is not recommended, unless the plant be used continuously for one and the same type of paste. It is true that the thermal efficiency of the direct steam injection method is the highest of all the heating methods, but the great drawback is that it is impossible to make exact allowances for the additional amount of water introduced into the batch by the condensation of steam. In those cases where it is really convenient, direct steam heating can, of course, be used in a jacketed vessel just as well as in an unjacketed vessel.

A thermometer arranged for external reading should be fixed on the mixer at the lowest practicable place.

To facilitate the operation of the plant and to economise in floor space, the various mechanical accessories such as the motor, the gears and the shaft speed change mechanism, should be fitted on one side of the mixer, mounted the one above the other.

The foundations for this accessory plant can be extended and serve as support for the graduated tank or vat for feeding solutions into the mixer. The vat may be constructed of wood, pitch pine for preference. A better construction, probably, is lead-lined sheet metal, since the vessel is mainly employed for cold, slightly acid solutions.

The pipe from the feed tank to the mixer should be of large diameter and arranged so as to have a slight, uniform fall. This feed pipe is extended into the interior of the mixer so that the liquid being added comes into immediate contact with the centre of the reaction mass.

The feed tank should be equipped with an externally-reading thermometer, and an open steam pipe for the rapid heating of the feed liquors to the desired temperatures at which they are to enter the mixer.

The mixer and feed tank may be lagged, of course, to prevent heat losses by radiation, but it is very doubtful, particularly with plant of comparatively small size, whether the saving secured warrants the additional cost of the lagging.

Powder Mixers.—Certain adhesive products, in particular casein glues, are sometimes prepared by simple admixture of the casein in powder form with the various powdered and sieved additional ingredients. The most useful type of plant for this purpose is the so-called "Turbulent" mixer, which consists of a simple square-sectioned box mounted on trunnions and fitted with a hopper to receive the finished product.

It would seem better practice, however, to adopt a cylindrical mixer fitted with blades of any convenient type, rotating at relatively high speeds. In such a plant, a homogeneous mixture is obtained

far more rapidly than in one of the "Turbulent" type. The horizontal single-shaft mixer-masticator described in some detail above is also perfectly suitable for making dry powders, provided arrangements are made for clamping on the lid tightly and for operating at a higher speed than in the case of solutions.

Driers for Desiccated Starch Adhesives.—It is sometimes desired to produce a starch-base adhesive, made by any of the wet processes to be described later, in the dry form. This process, of course, is one which interests only the large maker and shipper of adhesives and not so much the manufacturer who is making a product for his own use.

The drum drying method is in this case the most convenient. The paste is placed in a feeding trough, from which it is transferred by a series of subsidiary cylinders, in the form of a very thin film, on to the surface of the main cylinder, which is steam-heated and which rotates slowly. The dried film is removed from the cylinder by means of a scraper knife, the fragments falling into a trough and being carried away on a transporter band.

To facilitate the re-solution of starch adhesives that have been dried-out in this manner, it is advisable to make the original solution slightly on the alkaline side or to add such salts as sodium chloride, sodium sulphate, or sodium phosphate, with or without the further addition of wetting-out agents.

CHAPTER VI.

PACKAGES AND CONTAINERS.

For purposes within the works themselves, the most widely used and cheapest material for the construction of containers is galvanised sheet iron. Containers of this type are just as suitable for storing aqueous adhesive solutions as for solutions in organic solvents.

Owing to the tendency possessed by adhesive pastes to dry-out and to form surface skins, the lids of containers should not be of the flush or recessed type, and should possess a certain amount of play. Copper is too expensive as a constructional material, and tinplate not sufficiently strong. This latter point is particularly important in connection with starch adhesives obtained by treatment with a base or salts by the cold process, this type of paste coagulating rapidly by diffusion from the periphery of the container towards the centre, and thus occasioning considerable stress on the container.

For the transport of starch adhesives, the only suitable package is wood in the form of light barrels made of pitch pine or preferably of spruce wood. For larger quantities, petroleum drums may conveniently be used. Since these drums have already contained oily matter, the staves are more resistant to the stresses imposed by the alternate processes of filling with adhesive solution and the desiccation of such solutions. It is not advisable, of course, to run pastes obtained by the heat process directly into such containers.

The dextrin pastes are less sensitive to packing conditions ; metallic drums of corrugated sheet iron, varnished on the inside, and with a wide opening closed by a stopper can be used. Such a package is particularly interesting for export purposes. It is light, can be closed rapidly and the drying-out of the paste is minimised. It has one serious drawback, however—the lining varnish is easily scratched and in such cases, as usual, any rust formed tends to spread rapidly behind the rest of the varnish and eventually to loosen it. A light beechwood cask is not much more expensive and has the advantage of possessing a certain value when empty.

CHAPTER VII.

FURTHER GENERAL CONSIDERATIONS.

Now that the various elements of the problem of adhesives have been examined both separately and in their general relationship to one another, a commencement can be made on the systematic consideration of the subject. The aim of this present work is confined essentially to consideration of the direct production of cold adhesives by methods which are possible and easily accessible, not only to makers, for sale, but also to users, and by methods which are simple to control and which enable the production of low-priced products. The following topics are consequently either omitted or but briefly mentioned :—

(1) The ordinary hot glues, represented mainly by the usual joiner's glue. These materials require extensive and fairly complicated plant for their manufacture, and as the writer has already indicated, in his opinion their position is likely to contract rather than to expand in the general field of adhesives. Further, as the manufacture of ordinary glue is a very long established process, a number of books which deal very thoroughly with their production and use is in existence. The use of gelatins and ordinary glues in the manufacture of cold adhesives will, of course, be discussed in its due place.

(2) Passing reference only is made to a number of adhesive materials which possess drawbacks on account of their non-uniformity, colour, odour, etc., and which can be replaced very advantageously by one or more of the numerous varieties of starch adhesives. Sulphite cellulose waste liquor is an example of the class of material referred to here.

(3) Adhesives in powder form are not discussed except in those cases where they form a really important branch of the trade, for instance, the casein adhesives. The sole advantage in the production of starch adhesives in dry form resides in the economies secured in transport and packaging costs, but the bulk of these adhesives is made at works where they are actually to be utilised. The manufacture of starch adhesives in powder form is very costly when compared

with the low price of the original material. For instance, starch adhesives in powder form are sold at from three to four times the price of the original starch from which they are made. Further, if the materials are to be made in the dry condition, the selection of formulæ is distinctly limited, whilst in all cases superior results are obtained with a paste prepared and utilised directly than with the same paste that has been dried and re-dissolved. The simplest method of obtaining a cold starch adhesive in powder form is probably that given in the following formula.

Amylaceous Cold Adhesive Powder.

Starch, ...	96	Mix and heat for 2 to 3 hours on an iron plate at 45°-50° C.
Ammonium persulphate, .	4	

From a purely logical viewpoint, there seems little advantage in transforming an ordinary glue into a cold adhesive. Whenever this method is adopted, the glue loses most of its gelatinising characteristics by the influence of the chemical products added. This change is reflected both in an alteration in the adhesive properties of the substance and an increase in its cost, whilst other raw materials are particularly suitable to the manufacture of cold glues. One point that should not be overlooked is that in most cases the costs of processing remain the same whatever be the initial price of the raw material, and consequently lower raw material costs are inevitably reflected directly in the cost of the finished adhesive.

From the writer's own experience in the manufacture of cold adhesives, he has been led definitely to the following conclusions :—

1. From the standpoint both of economy and simplicity, the starches, particularly cassava starch, should be used as far as possible to meet the varied demands for adhesives, the products being cheap and suitable for most of the purposes for which cold adhesives are applied.

2. For adhesives of higher concentrations, the immediate starch conversion products, the dextrins, are most suitable.

3. For adhesives of high concentration and in which high mechanical strength is also required, the caseins are to be selected.

4. Finally, for joints where water-soluble adhesives present adhesion difficulties, or where special properties as regards flexibility and solubility, hardness, etc., are required in the film, the following are indicated :—(*a*) Rosin or equally cheap gelatinising materials. (*b*) Where rosin is impracticable, the water-miscible adhesives can be replaced by solutions of rubber, cellulose derivatives, synthetic

resins, etc., in organic solvents. In these cases, naturally, the price is higher.

5. The various raw materials should be transformed with the most generally available and cheapest chemical products as far as possible.

6. The various adhesives envisaged should be considered from the viewpoint of the material being joined and the methods of application.

As stated earlier, the writer's intention is to deal with the subject on general lines, and not to weary and confuse the reader with a multiplicity of formulæ. It is hoped, however, that the information presented is such that will enable the reader easily and rapidly to select a type of cold adhesive that most nearly meets the needs of any special case he encounters.

In general, the method of presentation of the individual cold adhesives has been so chosen that the cheapest ones are considered first, and the most expensive ones last, intermediately-priced products being valued very much in the order as given in the book.

Solutions and Dispersions.—With water-soluble cold adhesives, solution in water is naturally the method chosen for the preparation of their solutions, but the possibility of increasing the efficiency of such solutions by the addition of small quantities of any of the wide range of wetting-out agents now available should never be overlooked.

With adhesives which are insoluble in water, solution in organic solvents is generally adopted, but the industry is becoming steadily more alive to the possibilities of the application of such materials in the form of aqueous emulsions. The method of making such emulsions varies with the class of raw material used, which must in all cases before dilution and homogenisation be prepared in a semi-liquid or semi-pasty condition.

If the adhesive base can be heated without undergoing decomposition, it may be melted with the aid of heat; if the material does not melt, or if it decomposes at raised temperatures, it is brought into the desired semi-pasty condition by the aid of a small quantity of a suitable solvent. In either of the above cases, however, the final emulsion is obtained by the addition of water containing an emulsifying agent and a colloid normally stable in water. The effect of the emulsifying agent is both to reduce the surface tension of the liquid and to facilitate the dispersion, and the effect of the colloid (gelatins, caseins, starches, solubilised starches, dextrins, gum arabic, colloidal clay, etc.) is to act as a "protective colloid" and to stabilise the dispersion. In the preparation of such aqueous emulsions, the mechanical factor is frequently of great importance. Efficient stirring

and beating should be provided during the making of the emulsion, whilst final passage of the mass through a colloid mill, where possible, is always to be recommended.

The Colloidal Clays.—It will be noted that reference is made to colloidal clay among the " protective colloids " listed briefly in the last paragraph. The best known of the colloidal clays is the product bentonite, a material mined mainly in the United States and to a certain extent in Canada. This bentonite is a remarkable material which has already found extensive use in a wide variety of industries. It is a clayey product the individual particles of which are so minute that they are not visible even under the most powerful microscope. Unlike the particles of ordinary clay, the particles of bentonite are wholly colloidal, and when the mineral is mixed with an excess of water a permanent suspension from which the bentonite does not settle even on very long standing is obtained.

These clays possess many of the properties which characterise the colloidal gels, in particular those of swelling and becoming plastic when moistened. The degree to which bentonite can swell in water is in many cases very considerable. A product of such fineness that 99 per cent. passes through a 300 sieve will, when twenty grammes are mixed with a litre of water, produce a homogeneous suspension sufficiently rigid to prevent the fall of the particles.

The exact composition of the bentonites has not been ascertained, but they are probably mixtures of several substances, the main constituents being, most likely, china clay in very fine grain and actual colloidal silicates.

A refined bentonite has a density of about 2·78, softens at about 1,330° C., whilst it will absorb about five times its weight of water without showing any signs of containing moisture.

Owing to its efficiency, its cheapness and its stability at low temperatures, bentonite is an emulsifying and stabilising agent of particular interest to the maker of cold adhesives.

The incorporation of bentonite in an adhesive emulsion presents no particular difficulties. As with other products, the more rapid the agitation and the higher the temperature of the water, the more rapidly is the emulsification effected.

In every case where a dry, insoluble mineral powder is to be mixed with an aqueous adhesive solution the precaution should be taken of first moistening the powder with a little water, preferably containing a little soap to secure rapid mixing. If the powder be added in the dry state, owing to the avidity with which it takes up water, there is danger of the formation of small lumps which prove difficult to break down even on protracted mixing.

Formulation Quantities.—A note may be given here on the principles on which the various formulæ which follow have been based. The choice lay between taking a unit weight of the actual adhesive substance as the basis or adopting a unit weight of finished product. The latter alternative has been considered to have more in its favour, and most of the formulæ have been arranged for the production of 1,000 kilogramme batches of the various adhesives. Modification of the quantities of the constituents to give larger or smaller batches consequently is very simple.

CHAPTER VIII.

CHEAP STARCH-BASE ADHESIVES.

In this chapter on the starch adhesives particular attention will be paid, for reasons outlined in an earlier chapter, to products based on cassava starch, but those cases in which it is advantageous to make use of potato starch will be pointed out.

By simple hydrolysis, that is, by simple heating with water, the starches are converted into rather coarse pastes, of poor adhesive value and definitely unstable, the original starch grains simply being swollen. By the action of chemical agents, particularly the caustic alkalis and such salts as the soluble chlorides, the amylaceous granules are profoundly attacked and the various fractions—the amylose and more particularly the more resistant amylo-cellulose—enter more or less into solution, giving very adhesive and very tenacious pastes.

The processes for the manufacture of starch adhesives may be divided into two main groups: (*a*) Those in which the hydrolysis is effected in the cold with the aid of caustic alkali and which produce pastes of a viscous and ropy nature; and (*b*) those in which higher temperatures and oxidising agents are employed and which result in pastes of thicker and more compact nature.

It seems advisable at this point to controvert an idea which is quite wrong, but which seems to have met with fairly general acceptance among those manufacturing adhesives, and particularly starch adhesives, and that is that some distinctive value lies in the adoption wherever possible of a process that is carried out entirely in the cold.

It is true, of course, that the use of heat requires expenditure on fuel and water, but the heat hydrolytic processes offer a number of definite advantages. They are more rapid, the yields are higher and less supervision and less labour are required. Further, the cost of the chemicals is less and the adhesive solutions cost less to make.

With any particular type of cassava starch, if it is wished to make

paste of the lowest selling price combined with the maximum adhesive efficiency at that price, the heat hydrolysis method is the one to be selected. Again, starch pastes produced by the heat hydrolysis method are perfectly neutral and stable, and this is not always the case with pastes made by the cold alkali process, since these latter always tend to revert to a greater or lesser degree. Finally, these latter pastes always contain a rather high percentage of chemical products with hygroscopic tendencies which may tend to cause rusting of the containers, lead to the growth of fungi or moulds, or occasion other troubles. In the formulæ which follow methods are presented, however, for the avoidance of these drawbacks in cold-made pastes, but they are always likely to make their presence felt.

In the long run, every manufacturing problem with starch adhesives can only be solved in one logical manner: given the desired characteristics in the final paste, we have to decide which of the two main groups of processes is likely to offer the greatest net balance of advantages.

The modified starch can be used alone or with the following supports or fillers:

(*a*) Silicate of soda in the form of silica gel for adhesives of ropy consistency.

(*b*) Soaps for pastes of more compact structure.

(*c*) Neutral salts. These increase both the density and the viscosity of the pastes and produce a better eventual stability, but since their employment is invariably accompanied by enhancement of the hygroscopic nature of the paste, care should be taken that no greater quantity is used than is really necessary.

The utilisation of supports has already been mentioned in the sections on the adhesives problem and on the mechanism of adhesion. The advantage of their use does not reside only in cheapening of the costs of the starch adhesives, but also in the fact that they confer distinctive and desired properties upon the adhesives.

All that is essential in the manufacture of starch adhesives is discussed in the following pages. With the object of keeping the subject matter within reasonable limits it has been thought advisable to omit the experimental and other work upon which the various formulæ presented have been based.

Viscous and Ropy Starch Adhesives.—There are three principal modifications of the method for the manufacture of viscous and ropy starch adhesives by the cold process: (*a*) Treatment of the starch with moderately concentrated caustic soda, followed or not by neutralisation; (*b*) a similar treatment but with the utilisation of

sodium silicate in the form of silica gel; and (*c*) treatment of the starch with salts, particularly with calcium chloride.

Formula A-1.

Basic-type Formula for Soda-Starch Adhesives.

Water,	150	Mix.
Starch,	100	
Caustic soda, 36° Bé.,	25	Agitate for one hour to ninety minutes at a temperature of 15° to 20° C.
Water,	25	

When the starch is well thinned with the water, which does not take long, the alkali solution is sprinkled in without any special precaution. In a few minutes the mass changes into an opaque, very thick paste which, under the action of the mechanical stirrer soon becomes perfectly homogeneous, transparent, very viscous and tenacious. The time taken for completion of the process depends somewhat on the actual temperature and on the speed and efficiency of the stirrers, but ninety minutes may be taken as a fair average.

The actual quality of the paste improves with concentration of the solution, with the efficiency of the agitation and with the degree of accuracy with which the temperature is kept within the range 15° *to* 20° *C.*

There are distinct advantages in working in concentrated solutions. Not only is the paste of better quality, but from the viewpoints of cost of production and final value of the adhesive the reduced amounts of alkali and neutralising agents employed are very desirable features. Reduction of the percentage of the caustic soda solution on the weight of the starch to 22, with a corresponding proportionate reduction in the amount of water, yields a paste which is still basic in reaction. At the same time, the quantity of caustic given in Formula A-1 is that which allows of the easiest and most rapid mixing and which gives the most viscous product.

With too low a temperature, the activity of the caustic solution is reduced and the time of mixing is too prolonged. It is advisable, in winter, to work in a warm water- or steam-jacketed vessel. If it is necessary to make use of external heat to start the process, the fact that the process is exothermic, that is, that the reaction itself causes a slight temperature rise, should not be overlooked. If the temperature rises too high there is a tendency to the formation of dextrinised products and the final pastes will be less viscous and less stable than required.

Attention should again be drawn to the influence of the mechanical factor. If, as suggested in the chapter on plant, the mixer used is of the two-speed type, the lower speed should be used at the start of the process when the resistance to be overcome is very great. Usually after about half an hour the paste is thin enough to allow of the successful employment of the higher speed agitation—about 40 to 50 revolutions per minute. Working under these conditions the paste is well churned and steadily loses its gelatinous tendency to acquire a viscous and ropy condition. The mechanical factor will be examined from another angle in the chapter on strong starch adhesives.

Another alkaline material of distinct interest in starch adhesive manufacture under suitable conditions is *borax*, which possesses the property of effecting a considerable increase in the viscosity of starch solutions (Roger Dulac Processes). This effect of borax is very marked both on ordinary starch and on solubilised starch. The borax is used in the very low proportions of 1 to 2 parts per 1,000 of starch, or in the formulæ given below in the ratio of 1 to 2 parts per 10,000 parts of the total mass.

The adhesive solution treated should possess a minimum degree of basicity, or the borax will not exercise its desired effect of increasing the viscosity. By this use of borax the adhesive properties of the lower grades of starch are improved, whilst when working with all grades of starch, solutions can be obtained of greater dilution and at the same time of perfectly satisfactory properties than in the absence of borax.

If the quantity of borax employed is greater than the very small amounts specified above, there is a risk that, instead of the desired increase in the viscosity of the solution, coagulation will take place.

When the starch-alkali is made in concentrated solution the borax should not be added until the third stage of the process, with part of the water of dilution and before the neutralisation of the paste with acid. The practice of adding the borax at the very end of the operation is not so satisfactory. The best method of working is to add the borax to 8-10 times its weight of boiling water, to stir until solution is complete, and then to add the remainder of the water of dilution. Other interesting applications of borax in adhesives manufacture will be noted later in the case of the dextrins, casein and silicate of soda.

If a dextrin adhesive containing borax has been prepared in a mixer which is subsequently to be used for making a starch adhesive, the mixer should be very carefully washed out to avoid the possibility of

coagulation of the starch solution. The same remark applies, of course, to packages or other containers.

Adhesive solutions made by the formula and method just dealt with are too thick and too basic to be used direct. Whilst part of the soda is combined with the starch to form sodium amylate, there is always a balance of free alkali in the paste which, if unneutralised, would render the paste corrosive in many of its applications. Dilution and neutralisation with acid consequently is essential.

The neutralisation of a starch-alkali paste is always accompanied by an alteration in its adhesive properties, whilst the paste tends to lose its ropy consistency and to assume more of a gelatinous nature. It is advisable to leave the treated product slightly on the alkaline side. This ensures better keeping qualities, since means are present for the neutralisation of any acids eventually formed by fermentation, whilst the fermentation process itself is one which takes place less readily in a medium that is slightly alkaline than in one which is quite neutral.

Although, as just stated, a starch base adhesive solution that is too alkaline possesses an undesirable corrosive action in some cases, a paste that is slightly alkaline possesses definite advantages, particularly when it is to be used in connection with materials having a moisture-resistant surface, such as materials with a varnished or fatty surface.

Among the acids used for the neutralisation stage, hydrochloric acid (muriatic acid) easily comes first. It is efficient and cheap. Nitric acid is dearer and its use as a neutralising agent offers no special advantages. Phosphoric acid is still more expensive, but this material finds a certain specialised application in the production of the starch-latex adhesives which will be discussed later. If, for any particular reason, an adhesive maker does wish to use phosphoric acid for the neutralisation of ordinary starch products, preliminary trials should be carried out with small quantities, for it has been found that phosphoric acid from some sources has a distinctly coagulating effect upon the starch paste.

By working during the neutralisation stage strictly within the temperature limits maintained through the earlier stages of the process, the alteration in the consistence of the paste is kept to a minimum. Another point to observe is that it is preferable first to dilute the paste with the bulk of the water needed, and to add the acid at the end, mixed with a comparatively small volume of water, rather than to dilute the acid with the whole of the water and add the dilute acid solution directly to the thick paste.

Working by the methods discussed above, a semi-transparent,

slightly alkaline paste of somewhat ropy consistency will be obtained from the following formula :—

FORMULA A-2.

SLIGHTLY ALKALINE TRANSPARENT ROPY STARCH PASTE.

Water,	210	Temperature 15°-20° C.
Starch,	140	Mix the starch and the water.
Soda lye, 36° Bé.,	35	Add the alkaline solution and mix
Water,	35	for 60 to 90 minutes.
Water,	550	Add slowly at the beginning to
Borax,	0·140	dilute the paste.
Water,	50	Add slowly and regularly.
Hydrochloric acid, 22° Bé.,	5	

Ratio water : starch = 6 : 1.

The above combination represents the typical formula for this kind of adhesive.

We shall now consider a further type of starch adhesive derived directly from those given above but in which the neutralisation stage is accurately completed or where departure of the finished paste from neutrality is very small indeed. Under such conditions, since borax would not increase the viscosity of the paste, its use will be omitted, whilst the ratio water : starch will be slightly decreased, since both the absence of the borax and the exact neutralisation of the solution lead to a product of greater fluidity. If necessary, the viscosity of this type of adhesive starch paste can be increased somewhat by the addition of a solution of alum, which does not require alkaline conditions to exert its effect. Weight for weight, however, alum is inferior to borax as an agent increasing the viscosity of starch solutions, whilst the quantity of alum that can safely be used is small owing to the acid reaction which it gives to the paste.

With these neutral pastes, however, a new factor comes up for consideration, namely the use of *antiseptics*. Pastes that are markedly basic need no added preservatives, since bacteria do not flourish in distinctly alkaline media. But a neutral solution of a starch paste is almost an ideal culture medium for many types of micro-organisms and such a paste would not keep very long were not an efficient antiseptic added.

Of all the preservatives suitable for starch or dextrin adhesives, *formaldehyde* easily occupies pride of place because of both its cheapness and its efficiency. Other potent antiseptics such as benzoic acid, phenol, salicylic acid, thymol, salol, mercury salts, etc., offer no advantage over formaldehyde. They are usually more expensive,

and not superior to, if as efficient as, the aldehyde, whilst possessing numerous drawbacks in regard to colour, odour, secondary reactions, toxicity, etc.

No great case can be made out, either, for the very cheap antiseptics such as zinc chloride or sulphate, the efficiency of which for the purpose desired is not adequate. Zinc chloride, further, introduces undesired hygroscopic effects and the presence of either of these zinc salts is ruled out in many cases by the precipitation reactions that would occur during the making of the paste.

Formaldehyde solutions allow of the indefinite preservation not only of starch pastes but also of flour pastes which ferment even more readily owing to their content of albuminous matter. Formaldehyde solutions prevent not only the internal fermentation of starch and dextrin adhesive pastes, but also the growth of mould on their surfaces. The material can be used just as well in acid as in basic pastes and in neither case are any complications presented.

But the value of formaldehyde does not reside in its antiseptic efficiency alone. There is evidence that it forms some kind of chemical compound with the starch, the presence of which has a definite beneficial effect on the properties of the paste. The adhesive paste obtained with its use is clearer and more limpid, and its strength and water resistance after application is increased in all cases. This statement is made in the light of repeated dynamometer trials on the resistance to pulling apart of pieces of wood and of repeated trials on the resistance to degluing of test sheets coated with the pastes and immersed in water.

Formaldehyde is a gas obtained by the passage of vapours of methyl alcohol mixed with air over a metallic catalyst, usually silver or copper, at suitable temperature. Until comparatively recently, methyl alcohol, or methanol as it is now alternatively termed, was obtained solely as one of the products of the dry distillation of hard woods. To-day it is largely obtained by synthetic methods, the starting material being coal.

As a commercial product, formaldehyde solution is usually marketed in two strengths, namely solutions containing 30 per cent. of the actual aldehyde and solutions containing 40 per cent. It is the former material which finds application in the adhesives industry. In the more highly concentrated solutions the formaldehyde polymerises readily at low temperatures giving rise to trioxymethylene, a material which separates out as white insoluble crystals. To avoid this polymerisation, 40 per cent. formaldehyde solutions contain a certain percentage of methyl alcohol. Thirty per cent. formaldehyde solutions, however, are reasonably stable without any added methyl alcohol.

The following points should be borne in mind when using formaldehyde solutions in making starch and dextrin adhesives. In fixing upon the quantity to be used it must be remembered that part is lost by combination with the starch as described above and that a further portion is dissipated during the mixing of the adhesive, this latter loss depending upon the temperature and the duration of the operation. Too high a quantity of formaldehyde is equally to be avoided. It is not only a needless expense, but it gives an odour to the paste, whilst especially where female operatives are employed it is liable to give rise to irritation and dermatitis of the workpeople's hands. The more alkaline the adhesive paste the lower the quantity of formaldehyde it is necessary to use. Increase in the content of wetting-out agents which possess some antiseptic efficiency also reduces the quantity of formaldehyde needed. On the other hand, to ensure the preservation for long periods of fluid adhesives such as those which are rather highly diluted, the quantity of formaldehyde necessary is greater.

It should also be noted that with adhesives containing proteins, gelatin and casein in particular, formaldehyde exerts an insolubilising effect, and in such cases is used not for its preservative influence but because it improves the mechanical strength of the adhesive and because of its moisture-resisting properties.

The following is the type formula for a neutral, viscous and ropy starch adhesive :—

FORMULA A-3.

NEUTRAL VISCOUS ROPY STARCH ADHESIVE.

Water,	240	Temperature 15°-20° C.
Starch,	160	Mix the starch with the water.
Soda lye, 36° Bé.,	40	Add the alkaline solution and
Water,	40	mix for 60-90 minutes.
Water,	320	Add slowly at the beginning to dilute the paste.
Water,	200	Add slowly and regularly.
Hydrochloric acid, 22° Bé.,	31	
Formaldehyde, 30 per cent.,	5	Mix for 15 minutes.
Water,	5	

Ratio water : starch = 5 : 1.

On the weights, in kilogrammes, of starch and alkali given in the above formula, the quantity of acid to obtain a neutral paste is about 32 kilogrammes, but even in pastes of this type a very slight degree of residual alkalinity is advisable.

The neutralisation stage should always be controlled by the use of litmus, as the quantity of free soda present before neutralisation is dependent to a certain extent on the actual duration and efficiency of the paste mixing process. The formaldehyde solution is diluted before use with an equal volume of water to facilitate its distribution in the mass. It should always be added last and mixing not prolonged further than necessary, to avoid loss by volatilisation.

As has been pointed out, complete or almost complete neutralisation tends to occasion diminution in the viscosity of a starch paste (particularly if it is to be stored for any time) and imparts a tendency to gelatinisation.

Another factor entering into the manufacture of vegetable adhesives, namely the *salts*, will now be considered. These find three principal applications :—(1) In the direct production of vegetable adhesives, as will be discussed later. (2) As stabilising agents to minimise the reduction in viscosity of soda-starch adhesives, or to retard the reversion and setting of such soda-starch pastes as are produced by the hydrolysis process in concentrated solutions. This use also will be discussed later. (3) To increase the density, transparency, viscosity and ropy and syrupy nature of the adhesive.

As all the salts employed are characterised, to a greater or less extent, by their hygroscopic nature, care must be taken in their employment, and in general, not more than a certain maximum amount should be used.

The addition of an inert body to an adhesive paste of any kind means a certain weakening in film strength and therefore in resistance to tensile stress. Consequently, the salts are not used at all in the manufacture of the strong vegetable glues to be discussed in Chapter X.

The starch adhesives being considered in the present chapter are primarily the lowest-cost materials and their prices are usually lower, weight for weight, than those of the various salts that can be used. Consequently, the assumption should not be made in all cases that the cost of an adhesive will be lowered by the addition of mineral substances even though these latter are cheap enough.

Still, even with these reservations, the addition of salts to the cheap soda-starch adhesives is of decided interest when a paste of a transparent, ropy and agglutinant character is to be made. It should be noted in passing that these characteristics are a function of the density of a paste, that is, of its content of dry matter (adhesive substances or not), whatever be the type of adhesive in question. For instance, the starch adhesives now under consideration, and the dextrin adhesives to be considered in the next chapter, are made

with quantities of water ranging from 0·40 to 12 times the weight of the actual adhesive material. With high concentrations and a reduced viscosity, the micellæ, so to speak, slip over one another in the manner of a syrup. With low concentrations, this low viscosity, which would give a completely liquid glue, cannot be preserved and one is compelled, therefore, to make use of the gelatinising tendencies of the adhesive substance.

In the formulæ just given, the ratio of water to starch is about 5 : 1 and 6 : 1. The neutral salt added, since it does not possess any viscosity of its own, cannot increase the viscosity of the solution, but what it does is to furnish a saline stabilising solution which, by combining with the soda-starch, increases the density of the medium and gives the latter its desired physical properties.

Among the salts that can be considered as applicable normally with adhesives of this type, from the viewpoint of cost and ease of supply the following are the most important: Calcium chloride, sodium chloride, magnesium chloride, zinc chloride, sodium sulphate, zinc sulphate, disodium hydrogen phosphate, acid calcium phosphate and potash alum.

For a finished paste of the neutral type (Formula A-3) in which the effect of the salt is simply that of a stabilising and density-increasing agent, nothing better has been found than sodium chloride (ordinary salt). This gives a good transparent paste without any risk of precipitation even if the paste is not absolutely neutral. Its antiseptic value also is by no means negligible, it is cheap, easily obtainable and the least hygroscopic of the chlorides mentioned above. Further, as it is formed by the neutralisation of the excess caustic soda by the hydrochloric acid, it is already present in the normal paste of the type under consideration. Calcium chloride is very hygroscopic and gives a paste that is turbid and less viscous. Magnesium chloride possesses the drawbacks of the calcium salt to a higher degree, whilst it is more expensive. Zinc chloride finds a certain specialised application in the adhesives industry which will be mentioned later. Sodium sulphate is not hygroscopic, does not precipitate in slightly alkaline solutions, but gives less satisfactory results than does the chloride. Zinc sulphate, acid calcium phosphate and potash alum can be ruled out for various considerations. The use of sodium dihydrogen phosphate would be interesting, but its price is against it.

In regard to the quantity of sodium chloride that can be used, the following may be taken as guiding principles. If it is desired simply to improve the stability of the paste and to counter any tendencies to gelatinisation on neutralisation, whilst avoiding hygroscopic tendencies, 10 to 15 per cent. of sodium chloride on the weight

of the starch should be used. If relatively rapid drying of the paste is not indispensable, and if the greatest degree of improvement in density, transparency and ropiness is desired, the percentage of sodium chloride can be raised to 40 to 50 per cent. on the weight of the starch. The latter percentage is about the highest practicable. We arrive, therefore, at a type of paste of the following composition in which the quantity of acid used has been slightly increased so as to allow of the more accurate establishment of the point of neutralisation.

Formula A-4.

Neutral Saline Starch Adhesive.

Water,	240	Mix at 15°-20° C.
Starch,	160	
Soda lye, 36° Bé.,	40	Add and mix for 60-90 minutes.
Water,	40	
Water,	320	Add slowly at the beginning to dilute the paste.
Water,	200	Add slowly and uniformly.
Hydrochloric acid, 22° Bé.,	32	
Salt,	24	—Mix 10 minutes.
Formaldehyde solution, 30 per cent.,	5	Mix 15 minutes.
Water,	5	

Ratio water : starch = 5 : 1.

Before the sodium chloride is added, the paste should be tested with litmus paper. If the neutralisation point has been passed, that is if the blue litmus paper turns red, the paste should be corrected by the addition of 0·500 to 1 kilogramme of soda lye diluted with 8 to 10 times its weight of water. It may be recalled again that it is preferable in all these cases that the paste manifest a slightly basic tendency. As usual, the formaldehyde is added last, and it may be taken as a general principle in making all adhesives, that the antiseptic mixture be added to the batch at the latest possible moment in the process.

Comparative trials with adhesive A-4 and adhesive A-3 on glass sheets have shown that in cold and very damp weather the former dries rather more slowly, whilst it has a slight tendency towards crystallisation. This latter point is not of importance, however, as

adhesives of this type are not meant for high-strength joints. Despite its almost perfect neutrality, the paste made to Formula A-4 maintains its viscosity unimpaired and can stand considerable dilution.

A further interesting modification of the cheap soda-starch adhesives will now be described, this being also a cold process one, but wherein the ropy and transparent character of the products already described are modified, with the production of pastes which are denser and more opaque, notwithstanding the fact that they contain a higher percentage of water. In this modification, a special use is made of silicate of soda, or rather of *silica gel.*

If a dilute solution of hydrochloric acid be added to a dilute solution of sodium silicate, the silica is precipitated in the form of a jelly possessing a certain adhesive power. By the phenomenon of syneresis, this silica gel tends to flocculate and to liberate its accompanying water. If, however, the gel be produced not in water but in a starch-soda paste, the latter acts as the suspending medium, the result being a stable paste consisting of an intimate mixture of starch-soda and silica gel, very economical as an adhesive and permanent on storage for reasonably long periods.

These special pastes demand some care in making and handling since they tend to revert and lose their viscosity, this tendency increasing with rise in the percentage of sodium silicate used and decreasing with rise in temperature. Fortunately, in this case also, the stabilising properties of borax come to one's aid.

If products of very high dilution are to be made, it will be realised that at the beginning of a batch the quantities to be mixed are very small if the total volume of the finished paste is not to exceed the useful capacity of the mixer. There are, however, no really serious practical drawbacks to working under such conditions, even with a single-blade mixer. During the first few minutes, it is true, the starch-water mass tends to set into a block, but it assumes a viscous and ropy consistence very soon.

Once the soda-starch mass has been made, the immediate further addition of sodium silicate would thicken it more, and consequently it is preferable to dilute it first with a part of the water to be used. The subsequent addition of the borax is another reason for diluting the original paste before the addition of the sodium silicate.

The formulæ can be calculated from the following considerations:—(*a*) The soda-starch is prepared by the type A-1 formula. (*b*) The total quantity of water used, which is from 6 to 8 times the weight of the starch, is to be allocated as follows:—One part is used at the outset for making the starch-soda paste; a small quantity is used to dilute

the formaldehyde; the acid is diluted with 5 to 7 times its weight of water; the sodium silicate with 3 to 6 times its weight of water; and the remainder of the water is used to dilute the original paste before the introduction of the other products. (*c*) With a good starch, giving naturally a viscous paste, the best quantity of silicate is about one-third the weight of the starch. Below this quantity the paste will have more of the properties of the earlier ones described in this chapter. Above this quantity it will progressively lose in viscosity but increase in stiffness. (*d*) The borax should be used in the lowest amounts practicable, for reasons already mentioned. The actual quantity of borax will be the greater the higher the percentage of water in the paste. To secure the fullest advantage of the use of borax, the paste should contain about 1·50 to 2 kilogrammes of free 36° Bé. soda lye per 1,000 kilogrammes. If a paste is too closely neutralised, the borax is without action and the percentage of water in the paste will have to be decreased. This slight alkalinity of the paste is no drawback industrially. The following formula, A-5, is now given as a type of this paste in which the ratio of water to starch is 6 to 1, and Formula A-6 as a type in which the ratio of water to starch is 8 to 1.

Formula A-5.

Silicated Starch Adhesive.

Water,	200	Mix at 15°-20° C.
Starch,	130	
Caustic soda, 36° Bé.,	33	Add and mix for 60-90 minutes.
Water,	33	
Water,	200	Add slowly at the beginning to dilute the paste.
Water,	150	Add more rapidly, since the paste is now thinner. Finally mix for 15 minutes or longer to secure a very homogeneous product.
Sodium silicate, 35° Bé.,	43	
Borax,	0·100	
Water,	200	Add slowly and uniformly.
Hydrochloric acid, 22° Bé.,	35	
Formaldehyde solution, 30 per cent.,	5	Mix for 15 minutes.
Water,	5	

Ratio water : starch = 6 : 1.

Formula A-6.

Silicated Starch Adhesive.

Water,	150	Mix at 15°-20° C.
Starch,	100	
Caustic soda, 36° Bé.,	25	Add and mix for 60-90 minutes.
Water,	25	
Water,	230	Add slowly at the beginning to dilute the paste.
Water,	200	Add more rapidly, since the paste is now thinner. Finally mix for 15 minutes or more to secure a very homogeneous product.
Sodium silicate, 35° Bé.,	33	
Borax,	0·250	
Water,	200	Add slowly and uniformly.
Hydrochloric acid. 22° Bé.,	28	
Formaldehyde solution, 30 per cent.,	5	Mix for 15 minutes.
Water,	5	

Ratio water : starch = 8 : 1.

This type of silicated starch paste is very interesting. The pastes obtained are very cheap, very adhesive and dry rapidly enough. Owing to their high viscosity they stand further dilution, and can be preserved for months at a time even in winter. It is advisable and at the same time simpler to neutralise the soda, the silicate and the borax in one step. If pastes of types A-5 or A-6 in truly neutral condition are desired, the borax can be omitted and the quantity of water slightly reduced. Also, as in the case of adhesives of type A-2 and A-3, a weak solution of alum can be employed to increase the viscosity.

It should be stressed again though, that in all starch adhesives obtained by treatment with caustic soda, the neutralisation point should not be passed. A paste that has been treated with too much acid and then corrected by a further addition of soda, always possesses a viscosity somewhat lower than the same paste treated correctly in the first instance.

A method that can be used to avoid the possibility of the neutralisation point being passed is the following:—To the material in a slightly basic condition there is added a neutral salt which will react with any free alkali to form a precipitate. Such a salt is calcium chloride, of which not more than 5 per cent. on the weight of the starch should be used.

The following are the approximate neutralisation equivalents of the acids used :

850 grammes of 22° Bé. hydrochloric acid neutralise 1,000 grammes of 36° Bé. caustic soda solution.

250 grammes of 22° Bé. hydrochloric acid neutralise 1,000 grammes of 35° Bé. sodium silicate.

200 grammes of 22° Bé. phosphoric acid neutralise 1,000 grammes of 35° Bé. sodium silicate.

Technically, phosphoric acid is preferable to hydrochloric acid for the precipitation of silica gel, the gel obtained being in a better physical state than when precipitated with hydrochloric acid. The price of phosphoric acid is against it, however, and there are no practical drawbacks to the use of hydrochloric acid, especially when silica gel is precipitated in a starch medium.

The density and sticking power of the various adhesive starch pastes described in this chapter can be increased by the addition of sodium resinate, but this introduces a number of drawbacks and if more adhesive power and quicker-drying pastes are required, it is simpler and better to utilise the formulæ A-13, A-14 and C-1.

Numerous trials have been carried out by the author on the effect of various products as accelerators for the conversion of starch by the soda lye process, but the results so far obtained have not been of sufficient technical or commercial interest to warrant comment.

At the commencement of this chapter, mention was made of a third cold process for the manufacture of starch adhesives, namely by the treatment of the starch with a concentrated saline solution, in particular with a solution of *calcium chloride*. The basic type formula is given below.

FORMULA A-7.

CHLORIDE PROCESS STARCH ADHESIVE.

Water,	180	Mix at 20° C.
Starch,	100	
Calcium chloride (Flakes)	115	—Add and mix for about 2 hours.

In this case it is preferable to use a mixing temperature for the starch and water slightly higher than that in the caustic soda process, about 20° C. for preference. Although rather dearer than the fused product, it is advisable to employ the flaked form of calcium chloride,

which is so much easier to handle. The calcium chloride is added directly, and without any special precautions, to the mixture of starch and water.

The solution of the chloride in the water occasions a rise in temperature and under the conditions of the process the starch grains disrupt and enter into chemical reaction to some degree with the chloride. After about two hours' mixing and subsequent dilution, there is obtained an extremely agglutinant, very transparent, very dense and very syrupy paste.

Only calcium chloride is of economic interest for this purpose. As compared with magnesium chloride, it is less hygroscopic, cheaper and more effective. The manufacture of a paste of this type is extremely simple. No neutralisation stage is required, it sufficing simply to dilute the initial paste.

Borax can be used very advantageously to improve the viscosity of the paste and to allow of the use of a higher percentage of water. In pastes of this type, about 1 per cent. of borax on the weight of the starch can safely be employed. This is owing to the slight acid reaction of calcium chloride, which reduces the alkalinity of the borax. The final borax-treated paste has a slightly alkaline reaction, advisable for storage purposes and for the other reasons that have been given. The borax also exerts its usual supplementary antiseptic action. To be on the safe side, and especially when pastes of this type are to be kept for long periods and at summer temperatures, it is advisable to add a small quantity of formaldehyde. Formula A-8 gives the quantities for a complete finished adhesive paste of this type.

Formula A-8.

Chloride Process Neutral Starch Adhesive.

Water,	220	Mix at 20° C.
Starch,	120	
Calcium chloride (Flakes)	140	Add and mix for about 2 hours.
Water,	550	Add slowly at the beginning.
Borax,	1·200	
Formaldehyde solution, 30 per cent.	1·800	

Ratio water : starch = 6·4 : 1.

The type of starch paste made by the cold calcium chloride process and described above, finds its principal, and one might almost say its sole, employment in the manufacture of wallpapers, in which use

the hygroscopic properties of the dissolved salt are a distinct advantage. A typical paste for paper printing is made up of 20 parts of water, 20 parts of white substratum, 2 parts of pigment and 6 parts of the starch adhesive paste. This type of paste tends to retain a certain plasticity, and possesses an agglomerating power for mineral pigments superior to that possessed by pastes which give a perfectly dry film. The speed of drying of printed wallpapers is naturally slow, but the driers used in industry have been designed of size adequate to overcome this drawback.

The use of borax in starch pastes for the wallpaper industry is particularly beneficial, since its presence means a better conservation of the viscosity of the paste on mixture with the pigments and less tendency to lose this viscosity under the influence of the rotation of the printing cylinders.

Another advantage of this type of paste in the wallpaper industry is its suitability for working with metal powders, including aluminium powder. With an unsuitable paste, the application of these powders frequently fails, owing to defective adherence, or the powders lose their metallic lustre during or after application. Again, wallpaper which retains a little moisture is far more suitable for the purpose of the paperhanger than a paper printed with a well-drying paste and which becomes hard and somewhat brittle on storage.

For the manufacture of wallpapers, either a paste of the type described immediately above or one of the type A-3 may be used. It is difficult, however, to lay down hard and fast rules, but a little experimenting will soon ascertain the best composition of the paste for any particular job. Numerous trials have been carried out by the author on the effect of the addition of other materials on the hydrolysing power of calcium chloride in this process. It has been found that the quantity of calcium chloride can be diminished slightly if, instead of pure water, water containing a small amount of dissolved alum is used. A typical formula is A-9, below.

Formula A-9.

Chloride Process Starch Adhesive.

Water,	220	Use the water at 20° C. Dissolve the alum, add the starch, then the chloride and mix about 2 hours.
Alum,	2	
Starch,	120	
Calcium chloride (Flakes),	110	
Water,	500	Add slowly at the beginning.
Formaldehyde solution, 30 per cent.	1·800	

Since this paste has an acid reaction, the borax is omitted and the percentage of water of dilution reduced. Results with this A-9 material are improved by working in the presence of a little " Nekal " (an I.G. wetting-out agent), but it is doubtful whether the value of such additions is such as to outweigh the complications introduced.

The percentage of calcium chloride used can be diminished by working at higher temperatures, it always being understood that such elevation of temperature leads to a decrease in the viscosity, ropiness and transparency of the paste.

All the pastes described, obtained by the treatment at ordinary temperatures of starch with caustic soda or calcium chloride, can be manufactured from cassava starch or from potato starch, according to choice. In general, cassava starch is the more interesting material because it is cheaper and gives odourless pastes which are more viscous and transparent than those given by potato starch, though usually not quite so white.

Semi-viscous Starch Pastes (*Roger Dulac Processes*).—We now come to those processes for the manufacture of starch adhesives which are based upon the use of higher temperatures, with the help of bases and an oxidising agent. Manufacture by these processes is much simpler and more rapid than by the cold methods.

By raising the temperature of the mixture to 85° C., a complete series of pastes, ranging in concentration from about equal parts of water and starch to 12 parts of water to 1 part of starch, can be obtained. In other words, at the one end of the scale one can take the fullest advantage of the thickening power of the starch to obtain the cheapest adhesives, and at the other end of the scale produce highly dense and rapid-drying pastes usually only obtainable by means of dextrin and at much higher cost.

Manufacture of starch pastes by the hot processes is less delicate, as there are no " dangerous " materials to handle. The operations of neutralisation, etc., are omitted and the final pastes are more stable and dry more rapidly since they contain neither chlorides nor hygroscopic products. In all cases the film obtained on the drying of the adhesive is hard, flexible and dry, even in a humid atmosphere. The joints consequently are very resistant to moisture. Finally, the pastes obtained can be made more cheaply than those by the cold processes.

Pastes of this type are suitable for the great majority of the demands of industry. As made, they possess a good average viscosity and are capable of considerable dilution. They are not suitable, however, for such purposes as the wallpaper industry or other uses in which adhesives of very high viscosity are demanded. The products under consideration will be divided into three main types :—(1)

Ordinary adhesive pastes of high dilution ; (2) moderately concentrated pastes ; and (3) highly concentrated pastes.

In accordance with the usual practice throughout this book, mention will not be made of the details of the large amount of experimental work carried out by the writer and others, the main practical results alone being presented.

The processes are suitable both for potato starch and cassava starch, but the latter alone will be discussed owing to its especial advantages for this method. Cassava starch dissolves when it is attacked in hot solution by an oxidising agent (hydrogen peroxide for preference) in the presence of a base. For the first two of the three main types mentioned above, the alkali is 36° Bé. caustic soda to the extent of 0·450 kilogramme per 1,000 kilogrammes of mixture, and for the highly concentrated pastes is 6 kilogrammes of calcium hydroxide (hydrated lime) per 1,000 kilogrammes of mixture. 12-Volume hydrogen peroxide, which is the preferred oxidising agent, acts in a regular manner and produces pale and viscous pastes without the necessity of the excess oxidising agent being removed. The reaction differs according to the base utilised. Soda gives the palest and most stable pastes. With lime, the degradation of the starch molecule is more complete. Pastes made with lime, when raised to the boil, liquefy suddenly, usually with energetic decomposition of the hydrogen peroxide.

The quantity of oxidising agent used must be controlled, for if the amount employed is insufficient, the paste does not dissolve, whilst if too much peroxide is added, the paste tends to gelatinise. As a general rule, the quantity of peroxide necessary rises with the concentration of the paste being treated, but it also depends upon the degree to which the starch is to be attacked. Commercial hydrogen peroxide has usually a slightly acid reaction due to the presence of small quantities of material added for stabilisation purposes. The acidity of some makes of hydrogen peroxide is higher than that of others and the material, especially when it is to be used with intermediate-viscosity pastes, should be tested beforehand.

In the storage and handling of peroxide, certain precautions should be observed. It should be kept in a cool place and sheltered from light, whilst it should be protected against the accidental entry of impurities, for small quantities of organic matter falling into the peroxide may easily speed up its normal rate of decomposition. Storage of hydrogen peroxide in large quantities is not a procedure to be recommended either to the adhesives maker or any other comparatively small user. The peroxide can be weighed out into the same receptacle as the caustic soda, providing the mixed solutions are added

immediately to the batch, the peroxide otherwise decomposing rapidly in the presence of the caustic soda.

Improvement in the colloidal nature and stability of this type of starch adhesive, accompanied by improvement in actual adhesive properties, can be obtained by reduction of the surface tension of the product by the addition of a small quantity of ordinary white soap. The amount of soap necessary may be taken, in general, as about 0·5 kilogramme per 1,000 kilogrammes of paste. If more soap be used, the result will be unsatisfactory, the adhesive acquiring a pasty structure as distinct from the desired viscous one. The soap has another point in its favour in that it appears to augment the antiseptic properties of the preservatives used and consequently allows of a reduction in the quantity of the latter employed. The sulphoricinoleates are less suitable than ordinary soap, as they produce an " off-colour " paste. It has also been established in practice that such stable colloids as gelatin and gum arabic give less useful results than does soap.

The *preservative* recommended for this type of paste is a mixture of *sodium fluoride* and *formaldehyde* solution. Sodium fluoride is recognised as one of the best antiseptics in connection with vegetable adhesives. Its price is comparatively low, it is non-hygroscopic, stable and odourless. Its preservative effect is exerted over long storage periods, whilst its presence tends to increase the fluidity and ropiness of the adhesive. Formaldehyde solution, however, has an even superior preservative action, whilst the use of the two materials in conjunction is particularly serviceable, not only because they are quite compatible, but because the antiseptic value of a mixture of formaldehyde and sodium fluoride is definitely greater than would be assumed from the simple addition of the efficiencies of the two ingredients. There is a further reason in favour of the utilisation of this mixture. If such a mixture be added to a solution of starch paste containing hydrogen peroxide, the solution being at the boil or near the boil, the hydrogen peroxide decomposes extremely energetically and liberates its oxygen under conditions most favourable to the catalytic solubilisation of the starch. This decomposition is particularly energetic when lime is employed as a base. A small portion of the formaldehyde is oxidised into formic acid and neutralises almost completely the small quantity of soda lye used, the final paste having only the slight degree of residual alkalinity compatible with good keeping quality.

In all cases it is advisable to effect the liquefaction of the starch with the minimum of hydrogen peroxide and to obtain final pastes containing as little free peroxide as possible, otherwise further changes

continue on storage and the maker cannot rely on the consistence of the paste at the time it is to be used. As a general rule, a mixture of 2 parts by weight of sodium fluoride and 5 parts by weight of 30 per cent. formaldehyde solution per 1,000 parts by weight of finished adhesive paste is recommended. This mixture is satisfactory from the viewpoint of cost and properties of the finished pastes.

The mixture referred to has been tried out fully on test pieces of wood subjected to tensile strength trials and tests of behaviour on immersion in water. A starch paste is not, of course, usually employed for wood, but the test on wood is a useful and reliable one. It is also possible to use zinc sulphate as the preservative, this material being cheaper than the mixture of fluoride and formaldehyde, whilst it also is not hygroscopic. Experience has shown, however, that using equal quantities of preservative, the results are strongly in favour of the mixture.

If the paste is to be employed on tinplate, for instance on biscuit boxes, it is advisable to use a considerably higher proportion of sodium fluoride, the recommended mixture in this case being 6 parts by weight of sodium fluoride and 1 part by weight of 30 per cent. formaldehyde solution per 1,000 parts of finished paste.

Whilst the value of soap as a preventive of gelatinisation in a starch adhesive of this type is quite satisfactory so long as the final concentrations of the paste are not too great, with pastes of higher densities the use of soap alone is insufficient and the employment of neutral salts instead is to be recommended. With these higher density pastes, the improvement in transparency, viscosity and ropiness increases with the quantity of the salt used, it being still borne in mind that a simultaneous increase in the hygroscopicity of the paste is unavoidable.

By the use of salts it is possible, therefore, to produce by the hydrogen peroxide process, printing pastes of the type A-8, but with a lower ratio of starch to chloride. In this case the chloride is not, of course, the principal agent effecting the transformation of the starch, but merely an accessory product, modifying the final properties of the paste. The salts recommended are calcium chloride or sodium chloride, whilst soap and sodium fluoride are omitted to avoid precipitation possibilities. It is advisable not to use more than 10 to 15 per cent. of chloride calculated on the weight of the original starch, in order to keep the drying time of the paste reasonably low, particularly in winter and damp weather.

Either of the chlorides mentioned above may be used. Sodium chloride is, of course, a little cheaper, whilst it gives a rather lighter-coloured paste and has a certain antiseptic efficiency. Calcium

chloride gives a paste which is slightly less transparent but rather more agglutinant.

Using 10 per cent. of calcium chloride, the paste film, on drying, remains very homogeneous, whilst with the same quantity of sodium chloride tendencies to crystallisation are encountered. When the salts are used at a concentration of 15 per cent., it has been observed experimentally that the usual relation between sodium and calcium chlorides in regard to hygroscopicity are reversed, the effect in this direction of the former salt being slightly more marked.

On the whole, preference may be given to calcium chloride. These additions of salt are most useful if a concentrated adhesive paste is to be stored for considerable periods and at low temperatures.

The plant used for making starch pastes by the hydrogen peroxide process should be constructed of material such as copper if good-coloured products are required. Since the main advantage of this process is the production of a paste with good viscosity, the agitator can be worked at a speed reduced to about 10 revolutions per minute. It should always be remembered that a hot starch paste when too energetically mixed tends to lose its viscosity and to acquire a pasty character. The mechanical factor is in this case opposite to that obtaining in starch pastes made by the cold process, where energetic mixing is of definite advantage.

It should also be remembered that whilst in the preparation of starch adhesives by the cold processes the conditions of transformation and the results obtained are identical whatever be the quantities utilised, this is not the case when the hot processes are employed since, in the latter, the speed of heat transfer either in heating or cooling operations is dependent to a large extent upon the quantities of materials being handled.

When working with comparatively small batches, for instance between 50 and 100 kilogrammes, an ordinary jacketed pan is adequate, provided the steam pressure is good and the temperature can be brought rapidly to boiling point. The times of contact being relatively short, a quantity of hydrogen peroxide proportionately greater than with larger batches can be used, since the excess is rapidly removed during the ebullition of the mass. Prolonged agitating and heating, whilst improving the texture of the paste, in this case has no effect on its viscosity.

When working with larger quantities, batches of 1,000 kilogrammes for instance, it is advisable to work at temperatures not higher than about 85° C. and to diminish proportionately the percentage of hydrogen peroxide.

In every case, however, a certain amount of experimenting is called

for in the ascertainment of the quantity of hydrogen peroxide necessary to give the best results under any given condition of heating for a batch of the size decided to work. If the first trials give a paste which is too fluid after cooling, the quantity of peroxide is decreased in the next batch. If, on the other hand, the cold paste is too gelatinous, the amount of peroxide is increased.

The speed of cooling also is of importance. Too rapid cooling tends to give the paste a gelatinous character and, occasionally, quite a distinct difference in structure is encountered between that portion of the paste in direct contact with the walls of the pan and that towards the centre, which has cooled more slowly.

All these factors make it evident that results on the large scale cannot be relied upon to reproduce those of the small-scale batch formulation in the laboratory. To avoid the tendencies to gelatinise due to too sudden cooling, it is advisable to pour the glue into receptacles of a capacity not less than 25-30 kilogrammes.

Now that the general principles of the manufacture of starch adhesives by the hot processes have been discussed, representative typical formulæ for materials with contents of water ranging from 12 times the weight of the starch to equal quantities of starch and water, can be given. Pastes falling within this range meet the great bulk of industrial requirements, and all possess the advantages of cheapness, rapidity of drying, neutrality and freedom from hygroscopic effect.

Formula A-10.

Highly Diluted Starch Adhesive.

Water,	950	Heat to 85° C.
Caustic soda, 36° Bé.,	0·450	
White soap,	0·500	
Cassava starch,	80	
Sodium fluoride,	2	Mix for 15 minutes.
Formaldehyde solution, 30 per cent.,	5	
Water,	3	

Ratio water : starch = 12 : 1.

As, in this case, the fullest possible utilisation of the thickening power of the cassava starch is required, the hydrogen peroxide treatment stage is omitted. Cassava starch, by simple mixing with water, gives a fairly stable paste, but this stability is enhanced by the small quantities of caustic soda and soap present, and the antiseptics exert their usual preservative effect.

With cassava starches of French origin, which do not give pastes so viscous as do Dutch cassava starches, the further addition of a small quantity of borax is advisable.

A paste made according to Formula A-10 is exceptionally cheap and after cooling can support further dilution to a considerable extent.

Formula A-11.

Intermediate Concentration Starch Adhesive.

Water,	900	Heat to 85° C.
Caustic soda, 36° Bé.,	0·450	
Hydrogen peroxide, 12 vol.,	0·200	
White soap,	0·500	
Cassava starch,	110	
Sodium fluoride,	2	Mix for 15 minutes.
Formaldehyde solution, 30 per cent.,	5	
Water,	3	

Ratio water : starch = 8 : 1.

Formula A-12.

Intermediate Concentration Starch Adhesive.

Water,	850	Heat to 85° C.
Caustic soda, 36° Bé.,	0·450	
Hydrogen peroxide, 12-vol.,	0·350	
White soap,	0·500	
Cassava starch,	140	
Sodium fluoride,	2	Mix for 15 minutes.
Formaldehyde solution, 30 per cent.,	5	
Water,	3	

Ratio water : starch = 6 : 1.

In the two formulæ given above, which yield adhesives of higher concentration than does Formula A-10, borax cannot be used as the base, but both caustic soda and hydrogen peroxide are essential. In making up this paste, the agitator is set in motion and the various products added in the order indicated and without any special precautions. Steam is then turned on into the jacket of the mixer. The hydrogen peroxide decomposes slowly and regularly until the mixture of fluoride and formaldehyde is added. At this point, as has been stated earlier, the peroxide dissociates energetically. The paste obtained is fluid, free from lumps and can be poured into receptacles without sieving.

During cooling, a dry skin forms on the surface of the paste. This can be removed, or its formation can be avoided by immediately closing the casks and laying them on their sides.

When the same mixer is used to prepare, alternatively, pastes of the type now under consideration and dextrin base pastes of the types B-1 and B-2, discussed in the next chapter, it is necessary that the apparatus be washed out very carefully between each batch.

Formula A-13.

Concentrated Starch Adhesive.

Water,	750	Heat to 85° C.
Caustic soda, 36° Bé.,	0·450	
Hydrogen peroxide, 12-vol.,	3·500	
Cassava starch,	250	
Calcium chloride (Flakes),	37	Add and mix for 5 minutes.
Formaldehyde solution, 30 per cent.,	5	Mix for 15 minutes.
Water,	5	

Ratio water : starch = 3 : 1.

In this formula, owing to the lowness of the ratio of water to starch, the addition of calcium chloride is necessary to increase the translucent and agglutinant character and, particularly, the stability. The addition of soap and fluoride, since these materials are precipitated by the calcium chloride, is omitted. The quantity of calcium chloride used in this formula is limited to 15 per cent. on the weight of the starch, this quantity adversely influencing the speed of drying of the paste to the lowest practical degree.

Formula A-14.

Highly Concentrated Starch Adhesive.

Water,	600	Heat to 85° C.
Hydrated lime,	6	
Hydrogen peroxide, 12-vol.,	8	
Cassava starch,	300	
Sodium fluoride,	0·500	Continue heating for 15 minutes.
Formaldehyde solution, 30 per cent.,	1	
Sodium fluoride,	2	Mix for 15 minutes.
Formaldehyde solution, 30 per cent.,	5	
Water,	1	

Ratio water : starch = 2 : 1.

The adhesive paste made according to Formula A-14 being of the highest concentration, the use of caustic soda is abandoned in favour of hydrated lime, the action of which is more intense. It will be noted that the preservative mixture in this case is added in two lots, the object being to promote the energetic dissociation of the rather large amount of hydrogen peroxide used so as to obtain the greatest degree of oxidation and to prevent the transformation of the excess formaldehyde into formic acid.

It is even possible, by a slight modification of Formula A-14, to obtain a sufficiently fluid paste in which the weight of water is just equal to that of the starch but, on the whole, it is not advisable to go below the proportion of water given in Formula A-14, in which there is no danger of the paste made setting into a block even after moderately lengthy storage. By further bringing down the weight of water used until it just equals that of the starch, the colour of the paste suffers.

In making pastes of type A-14, it is preferable to work in small quantities so that they can be heated rapidly to the boiling point.

The addition of the first portion of the sodium fluoride and formaldehyde mixture is liable to cause considerable foaming and frothing, and the steam should be cut off until this has subsided.

The two adhesives prepared by Formulæ A-13 and A-14 are remarkably useful since they offer pale-coloured, rapid-drying and extremely economic pastes to industries using large quantities of such materials.

These starch preparations, made by the action of an oxidising agent, are not only useful as adhesives for ordinary purposes, but are equally valuable as sizes and finishes for the textile industry. Because of the extremely high degree of colloidal dispersion of the starch in these preparations, it is fixed not only on the surface of the fibres but actually in the fabric. The solutions are perfectly neutral, the small quantity of alkali used in their manufacture being combined with the starch, whilst the pastes are perfectly compatible with the other ingredients usually employed in textile sizes. If these latter-mentioned ingredients are soluble in water, however, it is preferable to add them to the finished starch paste ; otherwise they can be added during the manufacture of the original paste with the object of ensuring the highest degree of emulsification.

When applied to fabrics, sizes based on the starch adhesives under consideration give a high degree of firmness and lustre, without the undesired quality of stiffness. When applied to warps, the finished material is supple and elastic. In all cases the finishes are permanent and highly resistant to washing.

There are numerous further applications in the textile industry

of the particular type of solubilised starch product under consideration in this section. For instance, when employed as calico printing pastes they enhance the brightness and freshness of the colours obtained. Sizing preparatory to doubling, the sizing of silks and lace and the sizing of artificial silk filaments preparatory to winding may also be instanced.

In this textile field 90 per cent. acid ammonium sulphoricinoleate is of particular advantage as a wetting agent, giving results superior to those obtained with the neutral compounds. The value of this ammonium compound will be dealt with in more detail later.

The tobacco industry, and particularly the machine manufacture of cigarettes, is another important field for this type of solubilised starch adhesive. Three main types of adhesive are normally employed on these machines, namely the casein, the dextrin and the starch adhesive. The casein products are now but little used, since they are too basic and too liable to ferment with the production of an unpleasant odour. The dextrin products are excellent from the purely adhesive viewpoint on high-speed cigarette-making machines owing to their rapidity of drying, but they are always slightly coloured, are liable to give rise to a slight odour of burned sugar when the cigarette is smoked, and are too soluble. This last-mentioned drawback can prove very serious if the cigarettes are stored in even a slightly humid atmosphere. If a dextrin paste is employed in cigarette-making, however, it should be based on Formula B-10 (see page 103). Starch paste is the adhesive principally employed by the cigarette manufacturer, since this type of product does not discolour the paper, is cheap and most nearly approaches in chemical composition to the actual cigarette paper. Further, it gives joints satisfactorily resistant to moisture owing to the reversion of the paste.

Most cigarette manufacturers make their own paste, usually by the simple mixing of starch with water. The conditions of application, however, demand a very dense paste and, with the modern trend to the utilisation of ever-increasing speeds on cigarette-making machines, the demand is for pastes of still higher density and compactness of structure. This will be appreciated from the following brief description of the usual automatic process of cigarette-making.

After various preparatory treatments, which cannot be discussed here, the tobacco is placed in a large trough at the top of the machine. It is then combed out by a suitable arrangement and falls in separate fibres on to a paper ribbon curled up at the edges and which unrolls from a drum. The paper is carried by an endless belt and encounters a fine thread of paste distributed by discs. It passes through an electrical heating unit, where the paste dries and where the joint

is actually made. The emergent paper tube is cut into cigarette lengths by a circular saw, output usually being at the rate of 1,400 to 1,500 cigarettes a minute. The paste is originally fed into a cylinder, whence it is pushed by a counter weight or a screw to the pipe leading to the two discs which spread it on the paper.

The higher the speed of the machine, the greater is the necessity for high density in the initial paste to avoid too great a loss of consistence under the influence of the rotation of the distributing discs.

There are obvious drawbacks, therefore, to the usual simple type of starch paste. Its actual adhesive power is not very high; and as it ferments rapidly, it has to be prepared fresh every day, with the resultant loss in time. It is far preferable to prepare a true high-density and very adhesive paste according to the formula A-15 given below.

Formula A-15.

Special High-density Starch Adhesive for Automatic Cigarette Manufacture.

Water,	700	Heat to 85° C.
Caustic soda, 36° Bé.,	0·450	
Hydrogen peroxide, 12-vol.,	3	
Cassava starch,	280	
Hydrogen peroxide, 12-vol.,	1	Continue the heating until the fluidity of the product is correct.
Water,	3	
Sodium fluoride,	2	Mix for 15 minutes.
Formaldehyde solution, 30 per cent.,	5	
Water,	3	

Ratio water : starch = 2·5 : 1.

As the required product is to be very dense but not viscous, the latter property being a drawback from the viewpoint of the cigarette-maker, the relative proportions of water to starch must be kept low, and this in its turn means the utilisation of rather higher quantities of hydrogen peroxide than usual. The mixing should be continued until the batch is almost water-like in fluidity (after cooling, however, a very pale-coloured paste of lard-like consistence is obtained).

The actual quantity of hydrogen peroxide to be used when making-up this formula will vary slightly, of course, with the actual viscosity of the cassava starch employed, with the total weight of the batch and with the efficiency of the heating means.

It is better practice not to carry the oxidation and liquefaction of the starch too far, but to leave a slight residual viscosity and allow

stabilisation to take place by storage for some time in a cool place as is the usual practice with the dextrin adhesives. By making a completely liquid paste in the first place the adhesive can be used almost immediately, it is true, but its keeping properties are not too good, as it has a distinct tendency, particularly at low temperatures, to set into a block which is no longer serviceable.

A mixer made of copper, or lined completely or partially with this metal, is advisable if a very pale paste free from any trace of rust specks is desired.

The average-sized cigarette-making machine uses 1 to 2 kilogrammes of paste a day, and a convenient size for the storage receptacle for the pastes made by this process is about 25 kilogrammes.

It should be borne in mind that the solubilisation processes using oxidising agents that have just been described refer only to cassava starch. When applied to *potato starch* the processes fail, since the potato starch does not go into solution and does not lose its thickening properties to a degree allowing of the production of concentrated pastes. Instead, there is obtained a thick and lumpy paste which tends to revert and to separate its water of hydrolysis.

Is is possible, however, to adapt the processes to potato starch provided certain salts are used as the transformation agent. Zinc sulphate, zinc chloride, zinc oxide and even lithopone may be employed, but zinc sulphate has been found the most suitable.

Actually, the material which is used is the reaction product between an excess of caustic soda and the zinc sulphate, the product being known as sodium zincate. The effect of this material on the starch varies with the ratio of caustic soda to zinc sulphate, the higher the percentage of the latter, the more profound is the influence on the starch and the greater the loss in viscosity of the paste, the latter acquiring an opaque white colour. The higher the quantity of caustic soda, the greater is the degree to which the glue retains its viscosity but the more it tends to acquire a yellow shade. The following formula is suggested :—

FORMULA A-16.

SODIUM ZINCATE LYE.

Caustic soda lye, 36° Bé., .	100	Mix.
Zinc sulphate, . . .	20	

But even by adopting this method, the results obtained with potato starch are always decidedly inferior to those obtained by the methods based on cassava starch, and the employment of potato starch for the type of adhesives dealt with in this section is not really

recommended. Whenever potato starch is used, the resultant paste has a rather pronounced and somewhat unpleasant odour, which is never obtained with cassava starch. A further point is that adhesives made from potato starch seem to cool considerably more slowly than do those made from cassava starch. This is a point that should be noted, because when this type of paste is poured into containers of moderately large capacity, a distinct difference in the structure between the paste near the side walls and that towards the centre of the container is noticeable.

Cassava flour itself can be employed in place of the starch, which is naturally much dearer. Pastes made from the flour, however, are always less attractive in appearance than those made from the starch and cannot be obtained in high concentrations owing to the high percentage of cellulosic and other non-starch materials in the flour. If cassava flour is used, it should not only be of good quality, but also finely "bolted."

Adhesive pastes made from cassava flour always reveal tendencies to putrefy owing to their gluten content. By utilising the formulæ given on the previous pages, however, quite satisfactory preservation can be secured. The quantity of formaldehyde employed should be rather greater than when working with the cassava starch, although it should be noted that formaldehyde has a distinct tendency to cause the gelatinisation of the hot paste made from cassava flour.

Perhaps brief mention whilst on this subject should be made of the *ordinary flour paste*. This can be made with any type of flour. The flour is mixed with twice its weight of water and after a smooth paste has been obtained, 6 to 8 times the flour weight of boiling water is added. Flour pastes can be preserved with a little formaldehyde or, more cheaply, with zinc chloride. To prevent mould growth on the surface, the addition of a little benzaldehyde is recommended. This latter product is comparatively inexpensive.

Dense Thick Starch Adhesives (*Roger Dulac Processes*).—We come now to the next main group of starch adhesives, namely the thick and compact products which are essential for a number of industrial uses. Large quantities of starch-derived adhesives in a form as dense as possible and as little ropy as possible are demanded in industry, particularly in connection with paper and for either manual or automatic application. With these pastes, the call is for products which will adhere immediately and, particularly where automatic machines are employed, will obviate any danger of tickets, etc., sticking together, as would be the case were pastes of too high viscosity used.

Products of this type have already been mentioned in connection with the utilisation of silica gel in starch pastes, but the matter will now

be dealt with more systematically. Methods have also been given for reducing the gelatinous and viscous properties of cassava starch pastes in connection with cigarette adhesives, but in this particular instance the object was to make a paste of high concentration, price being relatively an unimportant matter.

To obtain a much cheaper thick paste, quite suitable for numerous industrial uses, the simple device can be adopted of imparting thickening power or " body " by the addition of ordinary white soap. The paste obtained is of excellent whiteness, neutral, non-hygroscopic, very stable, compact and eminently suitable for spreading.

If white soap (ordinary Marseilles soap) be dissolved in 10 to 15 times its weight of boiling water, there is obtained, after cooling, a transparent jelly which constitutes an efficient and economic support for a true adhesive solution. The soap in this case, being used in large quantities, functions as an actual thickener, its properties of reducing surface tension and of acting as a colloidal stabiliser being here of minor importance.

The proportion of soap used will vary with the quality of the cassava starch, but from 12 to 14 kilogrammes of soap per 1,000 kilogrammes of finished paste may be taken as an average. The soap should be added towards the very end of the paste-making process, just a few minutes before the addition of the antiseptic mixture. The temperature should not be allowed to exceed 85° C., for above this point the whole mixture tends to gelatinise.

In this type of paste, the quantity of formaldehyde used can be reduced and the fluoride can be omitted. A very economic paste can be made by Formula A-17 :—

FORMULA A–17.

DENSE SOAP-CONTAINING STARCH ADHESIVE.

Water,	880	Heat to 80° C.
Caustic soda, 36° Bé.,	0·450	
Cassava starch,	110	
White soap,	14	Add and raise temperature to 85° C.
Formaldehyde solution, 30 per cent.,	4	Mix for 15 minutes.
Water,	6	

Ratio water : starch = 8 : 1.

For the cheapest possible paste of this type, the fullest advantage should be taken of the thickening power of the cassava starch itself. For this purpose, as has been discussed earlier, only a slight addition

of caustic soda should be made and the use of hydrogen peroxide omitted.

With cassava starches of French origin, which are less viscous and less thickening than Dutch cassava starches, the amount of starch in the above formula should be increased a little, and the caustic soda be replaced by 300 to 350 grammes of borax.

It is sometimes required to produce a paste of this type of higher density and more agglutinant. For this purpose, Formula A-18, in which the quantity of water has been reduced to half of that in Formula A-17, can be employed. In this formula, the gelatinising power of the cassava starch is reduced somewhat by the caustic soda-hydrogen peroxide treatment, the percentage of soap remaining fixed.

Formula A-18.

Dense Soap-containing Starch Adhesive.

Water,	800	Heat to 80° C.
Caustic soda, 36° Bé.,	0·450	
Hydrogen peroxide, 12-vol.,	0·200	
Cassava starch,	200	
White soap,	14	Add and raise temperature to 85° C.
Formaldehyde solution, 30 per cent.,	4	Mix for 15 minutes.
Water,	6	

Ratio water : starch = 4 : 1.

A thick paste of this type can also be made with potato starch which, as already stated, gives unstable and lumpy pastes on simple cold hydrolysis. Instead of treating potato starch in the cold with a high percentage of caustic soda, followed by neutralisation with acid, the starch is made up into a paste with sodium zincate containing an excess of zinc hydroxide. Formula A-19 represents a potato starch paste made by this method.

Formula A-19.

Neutral Sodium Zincate Starch Adhesive.

Water,	950	Heat to 85° C.
Caustic soda, 36° Bé.,	13	
Zinc chloride,	20	
Potato starch,	80	
Sodium fluoride,	1	Mix for 15 minutes.
Formaldehyde solution, 30 per cent.,	3	
Water,	6	

Ratio water : starch = 12 : 1.

To obtain good solubilisation of the starch, the quantity of zinc chloride employed should be about 20 to 25 kilogrammes per 100 kilogrammes of starch. A temperature higher than 85° C. may be used in making pastes by Formula A-19 with certain advantages. A possible modification is the mixing of zinc chloride with the paste and the subsequent precipitation of zinc hydroxide in the mass. This means a better dispersion of the zinc hydroxide flocs, but the paste produced is less " bound " and this introduces complications.

Chloride of zinc alone does not possess anything like the solubilising activity of the same weight of neutral sodium zincate. Care should be taken that the zincate solution is as nearly neutral as possible for, if free caustic soda is present, the paste tends to turn yellow and to take on a more viscous character. If, on the other hand, zinc chloride is in excess, the keeping qualities of the paste are not so good and the paste has an acid reaction.

Since sodium zincate itself is quite a good antiseptic, the final addition of the sodium fluoride-formaldehyde mixture may be omitted, although it is advisable to use a little benzaldehyde to prevent the growth of surface moulds.

With potato starch, this process results in pastes which are very white, very dense and very adhesive. Made with cassava starch, the paste tends to discolour and to reveal gelatinous and elastic tendencies, although these latter can easily be countered by use of a slight excess of caustic soda and hydrogen peroxide. But when working with cassava starch, the sodium zincate method offers no real advantage and it is far better to rely on those methods employing a base and oxidising agent in conjunction.

There is one point in connection with these starch adhesives, and with adhesive solutions in general, that might finally be mentioned, namely, that susceptibility to fermentation usually increases with the dilution of the paste, and it may sometimes be advisable, when diluting, to add further quantities of antiseptics.

CHAPTER IX.

RAPID-SETTING DEXTRIN ADHESIVES.

THE methods described in the preceding chapter for the manufacture of starch adhesives have enabled the production of a series of materials with proportions of water descending from twelve times the weight of the starch used to twice the weight of the starch. For many present-day industrial requirements, these concentrations are too low to permit of rapid enough setting and drying. Industry to-day demands rapidity in fabrication, this being a matter of particular importance where, as is so often the case, the application of adhesives is effected by automatic means. The concentration problem acquires added importance when it is recalled that for many uses it is necessary to add further quantities of water to the initial adhesive to facilitate its application. Consequently, consideration will now be given to another starch-derived product, namely dextrin, by the employment of which, owing to its lower thickening power as compared with starch, it is possible to obtain the high concentrations desired.

The starches and dextrins constitute the " spear head " of the cold adhesives of the water-soluble type for all applications with the exception of the treatment of wood. Since, however, dextrin is distinctly crystalloid, it is not suitable for the production of high-strength joints. For this last-mentioned purpose use is made of the special transformed starches which will be the subject of treatment later in this book.

The dextrins, being obtained by the action of heat—either alone or in the presence of an activating agent—on starch, are never pure products in the sense that they consist of one single material. Their actual composition varies with the type of starch from which they are made, with the method adopted for its conversion, and with the degree to which the conversion process is taken. Between the initial product—the unaltered starch—and the final product, which is glucose, an almost infinite range of materials is obtainable.

At the one extreme, in ordinary practice, there are the white slightly transformed dextrins, which are essentially soluble starch, contain but a small percentage of matter soluble in cold water and which behave in many respects like the original starch. At the other

extreme there are the brown or pale dextrins containing a high percentage of glucose and almost completely soluble in cold water.

The following points should always be borne in mind: (1) The further the starch conversion process is taken, the more glucose does the dextrin contain and the greater is its solubility in cold water. (2) The colour of a dextrin deepens substantially in proportion to the degree to which its viscosity and thickening power diminish.

All the improvements made in the manufacture of dextrins for adhesives purposes have been with the object of obtaining a product which is completely soluble in the cold, as little coloured as possible, with as high a viscosity and adhesive character as possible, and free from glucose. Glucose, it should be remembered, is entirely without adhesive value and its presence even in small quantities produces dextrins which are hygroscopic. The presence of glucose in a dextrin is readily detected by means of Fehling's solution, and the same solution is employed for its quantitative determination.

The type of dextrin adhesive in greatest demand is one of high viscosity, low price and with a ratio of water to dextrin about 2 to 3. More concentrated and obviously more expensive adhesives are in request for extra rapid handwork and, more particularly, for automatic application. The most concentrated products contain about 40 parts of water to 100 parts of dextrin. In these last-mentioned special types the rapid-setting is secured by the low percentage of water in the adhesive, this water being partly absorbed by the material being glued and partly evaporated into the surrounding air.

Since the acid process is the one invariably employed for the conversion of starch into dextrin for adhesive purposes, the product always has a more or less pronounced acid reaction. The use of acids in the preparation of dextrin adhesives, whilst brightening the solutions, rarely improves their adhesive efficiency. More often it diminishes this efficiency, particularly when nitric, acetic or salicylic acid is employed. Further, an acidified dextrin adhesive can be the cause of serious trouble by its effect on the colour, strength, etc., of the treated material.

Treatment with alkaline materials, on the other hand, improves both the viscosity and adhesive effect of a dextrin preparation, although it also tends to darken the colour. As in the case of the starches, borax and caustic soda are the two chief alkalis used for the purpose. As a general rule it may be taken that alkaline media are used for dextrin adhesives of average concentration and acid media for adhesives of high concentration.

The effect of borax in increasing the viscosity of dextrin solutions is very pronounced indeed. As has been stated earlier, this effect is

most intense on slightly dextrinised starches and diminishes in proportion to the increase in the degree of dextrinisation. Consequently, with dextrin adhesives the quantity of borax required is higher than with starch adhesives, but the extra borax used has additional advantages. It increases the density of the solution, and consequently the speed of drying, whilst functioning as an inert filler and improving the stability of the adhesive paste. Further, borax is cheaper than dextrin. It is of advantage to make use of granulated borax, which is cheaper than powdered borax, whilst the latter also has a tendency to lump.

Caustic soda colours a dextrin paste more than borax does, but also confers upon it a vitreous, ropy and more sticky character. The presence of caustic soda also increases the solubility of the borax in the adhesive. The palest colour in a dextrin paste is undoubtedly obtained with borax alone, but the brownish discoloration produced by caustic soda is least pronounced in the presence of borax, whilst solutions of the greatest adhesive power are certainly obtained by the use of mixtures of the two alkalis.

When employing a combination of caustic soda and borax, the greater the degree to which the raw material has been dextrinised, the more adhesive is the resultant solution and the deeper is its colour. For the deodorisation of these dextrin adhesives, and to improve their colour a little, a small quantity of sodium bisulphite is added.

As in the case of the starches, prolonged heating and mixing, particularly when working with large quantities, alters the viscosity of a dextrin adhesive; a small laboratory sample prepared rapidly, possesses a viscosity higher than that of a paste made by exactly the same formula but on the large scale. It is advisable to work at a temperature not higher than 85° C., a heat sufficient to solubilise the original insoluble particles of the dextrin.

Reference to the question of the type of dextrin to be used in the production of adhesives was made in the chapter on Raw Materials. The three main types may, however, be listed as follows:—

Dextrin (*a*)—Ordinary slightly soluble dextrin.
Dextrin (*b*)—Ordinary soluble dextrin.
Dextrin (*c*)—Pale extra-soluble dextrin.

Whatever be the formula utilised, for the same reasons as were given in the case of the starches, dextrin adhesives tend to "revert," to lose their viscosity and to acquire a doughy and thick structure. This reversion tendency is most marked in highly concentrated adhesives and in those in which the degree of dextrinisation of the

raw material is least. At a certain point, however, the adhesive reaches a state of stability. At this point the soluble portion remains in solution in the manner of a solution of gum arabic and the insoluble portion tends to lump and to play the rôle of thickener in the mixture. The reversion process is favoured by low temperatures.

This state of affairs necessitates a certain compromise in practice. If an adhesive which is not completely liquid and which is to be utilisable immediately is desired, the percentage in it of slightly dextrinised starch is increased. This means that the reversion process is speeded up as far as possible. If, on the other hand, an adhesive reaching eventual stability and maintaining this state indefinitely is desired, a highly dextrinised raw material should be used. The adhesive which, just after making, is completely liquid, is then stored in a cool place for a month or two before being sold or used.

The above observations apply less to soda-borax dextrin adhesives which, as in the case of the starch products, are utilisable almost immediately, but rather to the highly concentrated low viscosity products.

Where a dextrin exactly corresponding to the type desired cannot readily be obtained, a satisfactory result can usually be effected by the judicious blending of two dextrins of opposite types.

There is, perhaps, one point which may be helpful to the buyer of dextrins. A maker who is capable of manufacturing a dextrin which is very soluble in the cold and which gives a very adhesive and only slightly-coloured solution—the most difficult type of dextrin to make—can usually be relied upon as being able to satisfy a user's requirements in any other type of the material.

Formula B-1.

Ordinary Dextrin Paste.

Water,	500	Make the dextrin into a thick paste with half the quantity of the water, add the rest of the water and heat to 85° C.
Dextrin (*b* type),	390	
Granulated borax,	46	Add successively, the bisulphite last, and bring the temperature to 85° C. again.
Caustic soda lye, 36° Bé.,	6	
Sodium bisulphite,	4	

Ratio water : dextrin = 1·3 : 1.

The addition of the water in stages is advisable, owing to the tendency of the dextrin to "ball" in the presence of much water.

Dextrin does not ferment readily—particularly if it is a slightly dextrinised product—and no antiseptic additional to that given in the above formula is necessary.

In order to keep down to a minimum the coloration obtained on prolonged mixing, and to obtain a better final viscosity, the caustic soda and borax solutions can be heated to 85° C. before their addition and the bisulphite added only a minute or two before the mixing is completed.

Although the above formula represents the simplest type of dextrin adhesive, it is possible to make one both better and cheaper by the admixture of starch. Potato starch is not suitable, since it does not give a homogeneous adhesive by simple hydrolysis; but cassava starch is suitable.

To prevent the coagulation of the starch by the borax it should be dispersed in the dextrin in the presence of an *emulsifying agent*, acid ammonium sulphoricinoleate, 90 per cent.—one of the range of commercial Turkey red or sulphonated oils—being exceptionally suitable for the purpose. This material improves both the stability and wetting power of the dextrin solutions, particularly on surfaces usually resistant to aqueous adhesives. Further, the employment of this ammonium compound facilitates the eventual deodorisation and decolorisation of the paste.

Soap and ordinary neutral ammonium or sodium sulphoricinoleate are distinctly inferior to 90 per cent. acid ammonium sulphoricinoleate. For the reasons that have been given in an earlier chapter, the addition of the ammonium compound named above is always advisable in dextrin adhesives, particularly those of the more concentrated types in which the various phenomena of colloidal dispersion, surface action, etc., are, so to speak, slowed down owing to the dryness of the product. The dispersing agent remedies this defect to a considerable degree, whilst it also assures a better initial mixing of the dextrin with the water.

The main interest of the following new formula (B-2) is that a part of the dextrin is replaced by cassava starch, which is cheaper and which gives a less brittle film than does dextrin alone (*Roger Dulac Processes*). Further, more than half of the soluble dextrin (*b*) can be replaced by the less transformed dextrin (*a*), the net advantage of the new formula being the possibility of increasing the viscosity of the adhesive solution, and consequently the amount of water that may be added to attain a definite viscosity, without in any way detracting from the adhesive value, any tendency to gelatinise being inhibited by the presence of the sulphoricinoleate. It will also be apparent that the paste will be much brighter.

FORMULA B-2.

ORDINARY STARCH-DEXTRIN ADHESIVE PASTE.

Water,	600	Mix the various constituents into a thick pulp with half the quantity of water specified. Add the remainder of the water and heat to 85° C.
Acid ammonium sulphoricinoleate, 90 per cent.,	2	
Cassava starch,	60	
Dextrin (*a*),	180	
Dextrin (*b*),	150	
Granulated borax,	46	Add the various ingredients successively, raising the temperature after each addition to 85° C. The bisulphite should be added last.
Caustic soda lye, 36° Bé.,	6	
Sodium bisulphite,	4	

Ratio water : dextrin = 1·5 : 1.

Starch being so much cheaper than dextrin, it is obvious that a method for the *direct production* of dextrin adhesives from starch offers considerable attractions. In discussing the manufacture of dextrins in the chapter on Raw Materials, that process depending upon diastatic fermentation was briefly dismissed, since it is not one that is suitable for actual manufacturers of dextrins for sale as such. The dextrin manufacturer markets his products in the solid form, and a manufacturing process which yields the materials in solution and requires expensive evaporating and drying stages naturally does not appeal to him.

From the viewpoint of the maker of adhesive pastes, the position of course is quite different, since the desired product is an aqueous solution. The direct manufacture of dextrin adhesives from starch naturally takes place in two steps: First, the preliminary transformation of the starch into dextrin; and secondly, the conversion of the treated starch into the adhesive by the processes described below.

On prolonged hydrolysis with water, starch is slowly converted into dextrin, and owing to the process taking place in aqueous medium the dextrin produced is invariably one containing a considerable amount of glucose. The speed of the reaction can be accelerated markedly by the use of a catalyst, and particularly by the use of the diastase *maltase*, extracted from germinated barley and the typical ferment for the breakdown of complex carbohydrates eventually into glucose.

Since starch is not a single substance, but a rather complex mixture, the components of which offer varying resistance to the process of saccharification, it is preferable to use as catalysts diastatic extracts which are themselves mixtures of ferments of differing degrees of

activity and which are met with in the trade under such names as " Diastafor," " Fermasol," " Rapidase," etc. The quantity of extract to be used depends upon its activity, and information on this point can be obtained from the suppliers.

The most favourable temperature for the diastatic conversion of starch into dextrin is 63° C. At lower temperatures the transformation is too slow, and with temperatures much higher the diastase is destroyed. It is highly necessary, therefore, to use a reliable thermometer, which should be so fixed that it can easily be read by the man in control of the plant. Again, owing to the sensitivity of diastatic ferments to materials acting as catalyst poisons, it is essential that pure materials be worked with. Failures with this process in the past have at times been definitely traced to neglect of this point.

It is, however, possible to improve the efficiency of the catalysts by the addition of very small quantities of *promoting agents*, the transformation being favoured by neutral or weakly acid conditions and retarded by alkaline conditions. In practice, the deleterious effect of alkali is most likely to arise from the lime frequently present in the starch. Another impurity in the starch leading to slowing-up of the diastatic conversion is the butyric-lactic acid mixture produced by fermentation during the solubilisation of the starch. The lime can be neutralised, however, and the production of butyric and lactic acids prevented by the addition of about one part per thousand of hydrofluoric acid, sulphuric acid or hydrochloric acid, which function as *zymo-exciters* or promoters of the catalysis at lowest practical temperatures for the process.

The most favourable temperature for conversion as given above, 63° C., is occasionally not high enough with certain starches, those of tropical origin in particular, these requiring a higher temperature for complete conversion into paste.

There are two other considerations in regard to this process which should be borne in mind. The first is that the more perfectly the starch paste is solubilised, the better and the more quickly do the diastatic ferments function. The second is that the speedier the transformation takes place, the better is the quality of the dextrin produced and the lower is the quantity of glucose the dextrin contains. In view of the various considerations outlined above, two different methods of technique come up for examination :—

(*a*) Direct heating of the starch with the catalyst. The water, the diastatic extract, the acid and the starch are put into the mixer and the temperature raised to 70°-75° C., according to the type of starch used, the pan being heated indirectly through its steam jacket until the paste which is at first thick becomes a limpid fluid. Heating by

the direct introduction of steam into the mass would mean a grave risk of destroying the catalyst.

(*b*) The catalyst is introduced into the finished paste and the latter cooled. This second technique is the more rational and the better. A small quantity of the water that is to be used is put on one side, the rest, together with the acid and the starchy material, being introduced into the mixer, the temperature of which is raised, whilst the mass is agitated, to 75°-80° C. This temperature is adequate for the complete hydrolysis of the starch grains into soluble form. There is no objection at this stage to direct steam heating; in fact it is a better and quicker method, although the additional water added by the condensation of the steam must be allowed for in the calculation of the original quantities of the batch ingredients.

When the paste has been made, the steam is shut off and the temperature of the mass reduced to 63° C. by adding water. The diastatic extract, diluted with the balance of the water, is now added and the temperature maintained in the pan by the passage of steam through the jacket.

The transformation must be stopped at the malto-dextrin stage and the further formation of maltose prevented as far as possible. Chemical control of the process is a matter of simple colour tests using as indicators potassium iodide solution and Fehling's solution. Starch and its conversion products up to the dextrin stage all produce distinctive colorations with iodine, ranging from deep blue to red-violet according to the degree to which the transformation has advanced. The test is not completely reliable if the solutions under test are warm, and consequently only a very small sample, which will cool quickly, should be removed from the pan for the test. The test with Fehling's solution is one which allows the definite and immediate ascertainment of the point at which the formation of glucose commences. Glucose gives no coloration with iodine, but on warming with a few drops of the Fehling's solution gives a red precipitate of cuprous oxide owing to its reducing effect.

Two simple tests are consequently necessary to follow the course of the process: (*a*) A small sample is treated in a test-tube with a few drops of potassium iodide solution and the moment when the coloration produced has passed from blue to red-violet is noted. (*b*) In a second test-tube, a similar small sample is treated with a few drops of Fehling's solution and heated carefully over a Bunsen burner. If a red precipitate is produced, commencement of the formation of glucose is indicated. Although somewhat lengthy to describe on paper, the test is essentially extremely simple and the knack of carrying it out easily acquired.

When conversion has reached the desired stage, part of the borax required by the formula is added to arrest the action of the catalyst, and the solution is heated to about 80° C. The remainder of the constituents of the adhesive, namely the borax, soda and the sulphoricinoleate, are then added.

It is advisable to introduce the bulk of the mixture of bases when the temperature has been raised to nearly 80° C. This minimises the tendency to discoloration which would be more pronounced if the alkalis were present during the raising of the temperature from 63° to 80° C., particularly if the temperature-rise were slow. If a very pale-coloured solution is desired, the use of the caustic soda lye can be omitted. It is also advisable to maintain the temperature of 80° C. during the addition of the alkalis, as too sudden cooling reduces the viscosity of the solution.

When small quantities of mineral acids are employed, it is essential that the quantities specified are not exceeded, otherwise, instead of activating the catalyst, they will reduce, if not entirely inhibit, its efficiency. Before heat is applied to the conversion mass, it should be tested to make sure its acidity is extremely low. The cases in which the use of these small quantities of acid is advisable are where the starches are derived from cereals grown on calcareous soils or where the process water is calcareous.

The difficulty in suggesting definite formulæ for the production of dextrin pastes on the method just outlined lies in the water figure, since the percentage of water to be used will vary with the nature of the starchy material, the viscosity desired, the system of heating employed and the temperature of the room in which the operation is conducted. It may be taken, however, that the product to be aimed at should contain from 130 to 150 kilogrammes of water per 100 kilogrammes of dextrinised starch.

Formula B-3.

Dextrin Adhesive Directly Produced from Starch.

Water,	600	Heat to 70° C.
Hydrofluoric acid,	0·050	Maintain temperature.
Diastatic extract,	0·200	Control transformation with indicator solutions.
Starch (or flour),	390	
Granulated borax,	46	Add one-fourth of the borax to stop the reaction. Heat to 80° C. Add successively the rest of the borax and the other products.
Caustic soda, 36° Bé.,	6	
90 per cent. acid amm. sulphoricinoleate,	2	
Sodium bisulphite,	2	

Formula B-4.

Dextrin Adhesive Directly Produced from Starch.

Water,	500	Heat to 75°-80° C.
Hydrofluoric acid,	0·050	
Starch (or flour),	390	
Cold water (approx.),	100	—Quantity sufficient to bring temperature down to 63° C.
Diastatic extract,	0·200	Maintain temperature and control reaction with indicator solutions.
Water,	10	
Granulated borax,	46	Add one-fourth of the borax to stop the reaction. Heat to 80° C. Add successively the rest of the borax and the other products.
Caustic soda, 36° Bé.,	6	
90 per cent. acid amm. sulphoricinoleate,	2	
Sodium bisulphite,	2	

Since dextrin, particularly in the presence of alkalis, is more or less soluble in cold water, a dextrin adhesive can be manufactured in *powder* form by utilising a very soluble dextrin and omitting the cassava starch.

Formula B-5.

Cold-Soluble Dextrin Adhesive in Powder Form.

Dextrin,	100	Mix.
Borax,	12	
Sodium carbonate,	1·200	

In use, it is necessary only to add the powder to about one and a half times its weight of water the evening before the day on which it is desired to use the adhesive. The solution obtained is of good quality, but from the viewpoints of efficiency, yield and price, the processes described earlier, utilising heat, are to be preferred. It is also possible, of course, to produce solid materials by the film evaporation of solutions over drum-type driers. The additional cost of this process, however, hardly compensates for any improvement in the solubility of the material.

Glucose itself can be used in adhesive pastes, not only to mitigate the brittle and friable character of the dextrins or to obtain pastes more suitable for tinplate, but also by itself in office pastes of the gum arabic type.

Formula B-6.

Glucose Liquid Office Paste.

Glucose,	100	Heat the water to 90° C. and mix until solution is complete.
Water,	50	
Borax,	50	

This paste may be thickened by the addition of a little soda lye, but at the expense of its clarity of shade.

Dextrin adhesives of higher concentration, that is, of the order of 40 to 50 kilogrammes of water per 100 kilogrammes of dextrin, are desired commercially as rather stiff pastes similar to honey in consistence and as little coloured as possible. To attain the latter object, reliance must be placed on the natural acidity of the dextrin itself. The extra addition of acids serves no good purpose and may even cause definite disadvantages. The viscosity and adhesive power of pastes of this type depend solely on the quality of the dextrin.

The addition of salts is not to be recommended since, owing to the low percentage of water in the paste, the presence of mineral salts would accentuate the crystalloid and drying-out tendencies of the dextrin. This effect is simple to verify on a sheet of glass. Two pastes of the same composition can be used, the one containing a salt and the other a slightly higher percentage of dextrin so as to have the same viscosity as the first. The superior adhesive behaviour of the latter paste can readily be demonstrated.

If for any reason it is desirable to use filling material in pastes of this type, the addition of disodium phosphate is recommended. A further useful material is salicylic acid in conjunction with borax in the proportions by weight of about 1 to 0·650. This mixture, which probably contains the salt sodium borosalicylate, has distinct antiseptic properties. Better results are obtained by the use of potassium oxyquinoline sulphate, which is an excellent antiseptic and wetting agent. Unfortunately, its rather high cost precludes its use in many cases. When it is employed, however, sodium bisulphite should not be used with it, otherwise the surface of the adhesive paste exposed to air becomes black. But when all is said and done, the increased thickening in the paste obtained by these additives can usually be obtained more simply by a slight extra addition of dextrin.

As to the type of dextrin to use, the points to be borne in mind are that slightly dextrinised products will yield a paste ready for use immediately, and that highly transformed and soluble dextrins yield pastes which require a more lengthy storage before equilibrium is attained. Usually, it is preferable to adopt the second type of dextrin.

Better than any of the additives described above, use can be made of the properties of formaldehyde solution to increase the transformation and the solubility of dextrins without darkening their colour and without altering their viscosity (Roger Dulac Processes). It suffices to heat the dextrin with 3 to 5 per cent. of 30 per cent.

formaldehyde solution to increase its degree of transformation. There are other modifications of this formaldehyde process, but these are of more interest to the actual dextrin maker than the adhesives manufacturer.

For the deodorisation and decolorisation of these highly concentrated dextrin pastes, the use of small quantities of sodium bisulphite is recommended for the cheaper qualities and of sodium persulphate for the better qualities made with pale soluble dextrins. Persulphate of sodium is an excellent decolorising agent, but its price is somewhat against it, whilst it gives rise to a rather abundant froth. Used in too great quantities it reduces the viscosity of the solution, but this is the case with all decolorising agents, hydrogen peroxide in particular having a marked effect on viscosity although as a decolorising agent it is very efficient. Probably sodium bisulphite is the best all-round material to use for this purpose.

It is also possible to avoid altogether the employment of chemical decolorising agents and the more or less pronounced effect on viscosity which they always produce, by the utilisation of a simple optical device. The addition to a paste of a very small quantity of high-class varnish-grade lithopone will alter the apparent coloration of a yellow or brownish product to practically a clear white. Care should be taken to avoid the addition of too much lithopone, which would detract from the viscosity and tend to give a dry paste. A safeguard against this undesired action of lithopone is afforded by the simultaneous presence of sulphoricinoleate (Roger Dulac Processes).

Zinc oxide is not suitable for this use as it produces a darkening, due to the acid medium. Before addition, the lithopone should be smoothed out carefully in a little water.

Formula B-7.

Highly Concentrated Dextrin Adhesive.

Water,	340	Heat to 80° C.
90 per cent. acid amm. sulphoricinoleate,	1·300	
Lithopone (varnish-grade),	0·330	
Dextrin (*b*),	660	
Sodium bisulphite,	3·300	Mix for 15 minutes.
Formaldehyde solution, 30 per cent.,	6·600	

Ratio water : dextrin = 0·50 : 1.

Formula B-8.

Highly Concentrated Dextrin Adhesive.

Water,	340	Heat to 80° C.
90 per cent. acid amm. sulphoricinoleate,	1·300	
Lithopone (varnish-grade),	0·330	
Formaldehyde solution, 30 per cent.,	20	
Dextrin (*a*),	330	
Dextrin (*b*),	330	
Sodium bisulphite,	3·300	Mix for 15 minutes.
Water,	7	

Ratio water : dextrin = 0·50 : 1.

Formula B-8 is derived from Formula B-7 and produces a paler and more adhesive paste than does the latter, since it utilises a dextrin which is less transformed, or a mixture with these characteristics, the solubility of which is enhanced by heating with 2 per cent. of formaldehyde solution, as indicated earlier.

It is sometimes necessary, for industrial use, to manufacture a very adhesive paste for delicate work which is to be both neutral and to contain only a small quantity of water. An example of such use is the jointing of two impermeable surfaces, one of which is fragile, between which the glue would be more or less imprisoned. An instance is the sticking of metallised labels used by perfumery manufacturers on their bottles. In such a case the dextrin can be neutralised with a little caustic soda. The presence of the sulphoricinoleate is retained to facilitate the adhesion to the glass, but other constituents except formaldehyde are omitted as a measure of caution.

Formula B-9.

Concentrated Neutral Dextrin Adhesive.

Water,	370	Heat to 80° C.
90 per cent. acid amm. sulphoricinoleate,	1·300	
Dextrin (*b*),	630	
Caustic soda, 36° Bé.,	3	Mix.
Formaldehyde solution, 30 per cent.,	6·300	

Ratio water : dextrin = 0·60 : 1.

A neutralised dextrin paste darkens in colour and possesses an adhesive efficiency inferior to that of the same product in an acid

or basic medium. It is essential, of course, that the quantity of alkali used should be no more than sufficient to neutralise, as determined by the litmus test.

FORMULA B-10.

EXTRA-RAPID-SETTING DEXTRIN ADHESIVE.

Water,	280	Heat to 80° C.
90 per cent. acid amm. sulphoricinoleate,	1·400	
Lithopone (varnish-grade)	0·350	
Dextrin (c),	700	
Sodium persulphate,	3·500	Mix for 5 minutes.
Water,	7	
Formaldehyde solution, 30 per cent.,	7	Mix for 15 minutes.

Ratio water : dextrin = 0·40 : 1.

As in this case the highest possible quality of dextrin adhesive is demanded, a pale, very soluble extra grade dextrin must be used, the quality of the paste depending entirely on that of the dextrin. The ratio of water to dextrin is about 40 per cent. and sodium bisulphite is replaced by sodium persulphate as a decolorising agent.

As in the case of Formula B-8, the expedient can also be adopted of utilising less-soluble dextrin which is converted into the desired condition by heating with 2 to 5 per cent. of formaldehyde solution. It should be noted that the transformation by means of formaldehyde is the speedier the greater the degree of dextrinisation of the material started with. With white dextrins, formaldehyde is not very efficient.

Pastes of the dextrin type are frequently employed in gumming by automatic means. When working on paper or tickets with a printed or varnished surface, it is useless to attempt to improve the adhesion by the addition of hygroscopic materials such as glycerin or of high-boiling water-miscible plasticisers such as glycol, diethylene glycol, diacetin, triacetin, triethanolamine, etc. The 90 per cent. acid ammonium sulphoricinoleate used in our formula is superior to any of these and, if necessary, a small extra quantity of this ricinoleate can be employed.

In the employment of adhesives of this class in automatic machines, it is frequently noticed that the work is less satisfactory in wet or damp weather, and in nine cases out of ten the trouble can be traced to the use in the paste of hygroscopic material such as glycerin that has been added to the paste with the idea of increasing its plasticity and combating its tendency to crystallise out. We must emphasise

again that better results can be obtained and defective adhesion in damp weather avoided, by using the sulphoricinoleate instead of glycerin.

The following special points should be noted in regard to dextrin pastes made expressly for the gumming of paper:

(1) The gum when applied should have a good affinity for water or saliva. It should consequently readily wet-out, and this means that its constituents should themselves be very soluble in the cold. Further, the more soluble the dextrin used, the brighter is the appearance of the gum when applied. In the formulation of pastes for this purpose, a very soluble dextrin should be used and its solubility enhanced further, without effect on its colour, by heating with 2 to 5 per cent. of formaldehyde solution.

(2) Although it has been stated above that glucose and glycerin are usually harmful in dextrin pastes, where these pastes are to be used for making gummed paper such materials may be admissible. They increase the polish of the gum film, whilst the glycerin counters the brittleness of the dextrin and gives a flexible dried film from the most concentrated solutions.

(3) Emulsifying or wetting-out agents should be added in very small quantities to facilitate the moistening of the gum.

(4) There is no need to use decolorising agents; they not only tend to render the gum more brittle but, by their use, make the gum layer appear thinner than it actually is, a point on which buyers may not be easily convinced.

(5) To obtain really satisfactory work it is advisable to counter the brittle character of the dextrin by the complementary addition of a soft adhesive, in particular, gelatin. This last-mentioned material has the further advantage of increasing the viscosity of the paste and preventing absorption of the gum by dark and insufficiently sized papers. The following formula, B-11, is given as a type formula, although everything depends upon the nature of the dextrin utilised and the price at which the gum is to be marketed.

Formula B-11.

Dextrin Adhesive for Paper Gumming.

Water,	600	Heat to 80° C.
90 per cent. acid amm. sulphoricinoleate,	0·400	
Formaldehyde solution, 30 per cent. (optional),	12	
Dextrin (c),	400	
Gelatin (optional),	20	Mix for 15 minutes.
Glycerin,	40	

The quantity of sulphoricinoleate may be reduced still further. The treatment with formaldehyde can be omitted with very soluble dextrins, although it permits the utilisation of cheaper dextrins. The quality of the gelatin material can vary from ordinary joiners' glue to very fine, pale, edible gelatins. The gelatin should be swollen first in cold water and added at the end of the paste-making process. The glycerin need not be of pharmaceutical quality but a good commercial grade should be employed. The higher the percentage of glycerin used, the stickier will be the character of the film, and the greater the risk of the envelopes, etc., sticking together if stored in a damp place. In practice, it is simple enough to find a dextrin paste to meet any paper-gumming problem by varying the quantities of sulphoricinoleate, gelatin, formaldehyde and glycerin.

CHAPTER X.

STRONG COLD ADHESIVES.

Strong Starch-basis Adhesives (*Roger Dulac Processes*).—The term "strong glues" is applied commercially to adhesive compositions possessing particularly marked agglutinant properties and high speed of drying, and producing a dry film which possesses a degree of mechanical strength equal to, or even greater than, that of the material being joined. It is further understood that the adhesive film shall not be capable of being readily removed.

The casein adhesives which will be discussed later in this chapter may be taken as typical of the strong cold glues. They possess a very good resistance to shearing stresses and to moisture—superior, indeed, to the hot glues—but they have two drawbacks. The first is their comparative instability; casein solutions should not be used longer than 12 to 24 hours after they have been made. The second is that their too high degree of free alkalinity is conducive to the formation of stains. Their price is also against them for some applications.

It is essential in these strong cold glues that there should be no hygroscopic material present and that the quantity of water contained should not be more than double the weight of the dry material, this being the usual proportion in casein glues.

We have stressed in the preceding chapters and, we think, have made out our case, that the starches constitute the most generally applicable materials for cold adhesives of all types, because of their cheapness, their abundance and the many different forms into which they can be converted. We will now try to justify this viewpoint once again by giving a process which permits of the manufacture from starch not only of "strong adhesives" but also of very pale and very adhesive products capable of replacing in numerous instances the dextrin adhesives described in the immediately preceding chapter.

In the attempt to produce from starch an adhesive solution with the properties of casein adhesives, it is essential that the cold processes be used, as those starch conversion methods based upon the utilisation of higher temperatures give an entirely different type of product.

The conversion process, in brief, consists in treating starch,

particularly cassava starch, with caustic soda and an oxidising agent—hydrogen peroxide—and then with sodium bicarbonate, which acts as a catalytic decomposing agent, the slight residual basicity being neutralised, if desired, by an acid or a solvent. Under these conditions the amylocellulose portion of the starch granules enters more fully into solution and the conversion of the sodium amylate is more profound. This latter change is reflected by a decrease in the basicity of the medium and by the direct production, after an adequate reaction period, of a finished adhesive paste without the necessity for any further dilution with water. This finished adhesive solution can be spread easily, is colourless, odourless and transparent, and possesses quite remarkable characters as regards viscosity, stickiness and tenacity. If one immerses one's hands in a paste of this type one finds the greatest difficulty in washing them clean again, for the paste, although soluble in caustic soda, dissolves in water only with difficulty. Joints made with this glue are not only very strong, therefore, but also waterproof.

One of the interesting points about the process is that it allows of the rapid obtaining of a liquefied starch with the minimum quantity of caustic soda. It can be claimed that the product is virtually a "vegetable casein glue." Compared with an ordinary casein glue it has the same percentage of water, the same physical characteristics and shows the same industrial results except, perhaps, in resistance to degluing. On this last-mentioned point the true casein glues are slightly superior, although the starch product is better than the hot glues, and in any event possesses the outstanding advantages over casein glues of being much cheaper and of much greater stability on prolonged storage.

It is true that the formula to be given yields a glue with a basicity higher than that of a normal casein glue, but it is easy to correct this without altering the properties of the starch adhesive, such correction not being possible with a casein glue. The actual method of neutralisation to be adopted depends upon the exact type of adhesive it is required to make and, from the economic aspect, if a dextrin-type product of the class given in Formulæ B-1 and B-2 is wanted, then neutralisation is effected with a little phosphoric acid or dilute hydrochloric acid. If, however, the paste is to be a casein-type material, and quality is to be maintained to the utmost, then what is recommended is the addition of *acetone* to the extent of 10 to 15 per cent. of the weight of the starch. Under the conditions existing in the paste, the acetone functions virtually as a neutralising agent for the free alkali, what actually happens being that a starch acetate type of compound is formed by the joint action of the caustic soda

and the acetone on the starch. The quantity of acetone used is insufficient to make the paste inflammable, but the paste becomes very white, opaque and creamy—very similar to a casein paste and quite neutral. The film left by this paste is very plastic, soft and transparent, whilst the absence of any apparent grain is visible demonstration of the high degree of solution of the original starch granules.

This acetone process at once calls up the possibility of utilising carbon bisulphide instead, with the formation of a starch xanthogenate analogous to the cellulose xanthogenate formed in the viscose process of making artificial silk. The use of carbon bisulphide in these adhesive pastes has, in fact, been tried with quite excellent results, but it is necessary to use the paste within a day or two after manufacture. On further storage it becomes too fluid and its viscosity falls to a point too low to ensure satisfactory results when applied to the gluing of wooden surfaces. Further, the paste turns yellow and its odour, bad enough at first, becomes worse. The higher the temperature, the greater the rate of this undesired decomposition. As compared with acetone, carbon bisulphide is cheaper, but the strongest argument against its use is its high degree of inflammability, making it a really dangerous product to employ, especially in workrooms full of combustible materials such as paper or wood. It should not be overlooked, further, that in the United Kingdom, the storage and use of carbon bisulphide is subject to Home Office regulations.

This new type of starch product can not only advantageously replace casein and dextrin products in numerous adhesive uses, but offers distinct possibilities in other avenues of application. It may be used, for instance, as the base for photographic emulsions, and in connection with transparent cellulose films, latex, etc., with economically satisfactory results.

If a starch adhesive of this new type is to be judged mainly for its plastic properties, no additional mechanical treatment is necessary, but if the fullest advantage is to be taken of its agglutinant properties, final treatment in a colloid mill is highly desirable, the product then obtained being a true "strong wood glue," colourless, cheap, neutral, extremely sticky and which pours like a very thick syrup. This final treatment in a colloid mill is not absolutely essential, even for making a wood glue, but it does give the final touch, although it naturally means an added, and not inconsiderable, item in production costs.

The usual type of *colloid mill*, it might be mentioned, consists essentially of two circular horizontal discs grooved concentrically and fitted with removable pegs or pins. The upper disc is fixed and

contains at its centre the feed hole for the supply of the paste being treated. The lower disc rotates at about six thousand revolutions per minute. The paste entering the machine is projected violently, by centrifugal force, against the pins and is disrupted into almost molecular condition.

Treatment of highly viscous and adhesive products in a colloid mill occasionally presents difficulty, but provided the feed is maintained regularly at a rate equal to the capacity of the machine, the handling in such a mill of the products made by the cold treatment of starches is fairly trouble-free. The colloid mill, it should perhaps be made clear at this point, is quite unsuitable to starch adhesives made by the hot processes, for these latter products, under the working conditions of the mill, tend to dry out and choke the space between the discs. Even when a colloid mill has been used for the cold-made starch products it should be cleaned out with hot water immediately after use.

Better results would probably be obtained in the cone type of colloid mill than in the pin type, the emulsification in the former type being obtained by the rolling and spreading of the material being treated between fixed and rotating surfaces, the clearance between these surfaces being very small indeed.

The possibility of the direct and complete manufacture of these very strong starch adhesives by simple passage through the colloid mill is doubtlessly attractive, but unfortunately such a process would offer considerable difficulties in practice.

To come now to the actual details of the manufacture of this new type of starch-derived strong glue, the original starch paste can be made by methods described earlier in this book, for instance :—

Cassava starch, . . .	100	Mix.
Water, ...	150	
Caustic soda lye, 36° Bé., .	25	Add.
Water, ...	25	

The quantity of bicarbonate of soda to use is 2 kilogrammes per thousand kilogrammes of starch, or 2 kilogrammes per three thousand kilogrammes of final paste.

It is difficult to give any hard-and-fast rule on the quantity of hydrogen peroxide to employ ; so much depends upon the original viscosity of the cassava starch, on the time of contact, on the actual temperature, and on the efficiency of the mixing blades. Probably 3 parts of 12-volume hydrogen peroxide per 100 parts of starch is the quantity that may best be taken as the basis for trial. In practice it is easy to tell whether the right amount of peroxide has been

employed. If too little has been used, the paste is too thick; if too much, the paste is ropier than desired. In the former eventuality more peroxide can be added and the mixing continued until the desired consistence is obtained.

About twelve hours should be allowed for the actual mixing, and the temperature should be kept between 15° and 20° C. The higher the temperature the more rapid the reaction, but at the expense of the quality of the paste. The essential point is to ensure that the liquefaction of the starch is brought about by the oxidising treatment and by the mechanical working, not by the temperature.

The value of the adhesive, its fluidity and its stability can be further increased by the action of an emulsifying agent, in particular 90 per cent. acid ammonium sulphoricinoleate in the proportion of 2 parts per thousand parts of starch. This addition is particularly desirable if the paste is to be given a final treatment in the colloid mill.

As to the plant necessary, a mixer with two speeds, with arrangements for bottom emptying and driven directly by an electric motor through laminated resinoid gearing, such as was described in an earlier chapter, will be found very suitable.

The various ingredients of the batch are added in the order given in the formula (C-1) and without any special precautions. Charging is conveniently effected in the evening and, after about thirty minutes, the high-speed stirrer started up. In the morning, provided the man in charge of the plant has watched the temperature carefully, and there have been no lengthy stoppages, the adhesive paste should be found quite satisfactory, very agglutinant, of syrup-like consistence and spreading to perfection. The paste can be passed directly to the colloid mill if this final treatment is to be given.

For use in connection with wood it is perhaps advisable to use these glues as fresh as possible. The final addition of formaldehyde is useful both to improve the keeping properties of the paste and to increase its strength and resistance to water.

Formula C-1.

Starch-derived "Strong Glue" (Dextrin Type).

Water,	420	Mix the starch and water with the bicarbonate and add the hydrogen peroxide, maintaining the temperature at 15°-20° C. during the process.
Sodium bicarbonate,	0·550	
Cassava starch,	280	
Hydrogen peroxide, 12-vol.,	9	
Caustic soda lye, 36° Bé.,	70	Add, and mix for about 12 hours.
Water,	70	

90 per cent. acid amm. sulphoricinoleate, . . .	0·550	Mix.
Water, ...	100	Add slowly.
Hydrochloric acid, 22° Bé., .	50	
Formaldehyde solution, 30 per cent., ...	5	Mix for 20 minutes.

Ratio water : starch = 2·1 : 1.

This type of adhesive paste is capable of replacing, for most uses, the dextrin adhesives given in Formulæ B-1 and B-2, whilst it has the advantages of being paler, more adhesive, capable of standing a higher degree of dilution and, of course, cheapness.

Care should be taken not to put this paste into containers or machines which have previously been dealing with pastes containing borax and which have not been thoroughly cleaned out, for if any trace of borax is present, paste of the type C-1 will coagulate immediately. This latter paste, it will be noted, is slightly on the alkaline side, always advantageous from the viewpoint of keeping properties.

Formula C-2.

Starch-derived "Strong Glue" (Alkaline Wood-glue Type).

Water, ...	500	Mix the starch, water and bicarbonate, and add the hydrogen peroxide, maintaining the temperature at 15°-20° C. during the process.
Sodium bicarbonate, . .	0·650	
Cassava starch, . . .	320	
Hydrogen peroxide, 12-vol., .	10	
Caustic soda lye, 36° Bé., .	80	Add, and mix for about 12 hours.
Water, ...	80	
90 per cent. acid amm. sulphoricinoleate, . . .	0·650	Mix for 20 minutes.

Ratio water : starch = 1·8 : 1.

Formula C-2 constitutes, from the viewpoint of viscosity, strength, ease of spread, simplicity and cost, the perfect type of "wood glue." Its free alkalinity is still a little higher than that of a normal casein glue and may, in rare instances, give rise to staining troubles. In cases where there is no risk, or little risk, of staining, the above formula is confidently recommended, as the paste made will be found to meet every other requirement. The film dries rapidly, but leaves sufficient thickness between the two surfaces being treated to assure perfect joining. Owing to its slight residual alkalinity, this paste tends to become yellow and to lose its viscous and honey-like character with rise in temperature.

FORMULA C-3.

STARCH-DERIVED "STRONG GLUE" (NEUTRAL WOOD-GLUE TYPE).

Water,	500	Mix the starch, water and bicarbonate, and add the hydrogen peroxide, maintaining the temperature at 15°-20° C. during the process.
Sodium bicarbonate,	0·650	
Cassava starch,	320	
Hydrogen peroxide, 12-vol.,	10	
Caustic soda lye, 36° Bé.,	80	Add, and mix for about 12 hours.
Water,	80	
90 per cent. acid amm. sulphoricinoleate,	0·650	Mix for 20 minutes.
Acetone,	38	
Formaldehyde solution, 30 per cent.,	6	

Ratio water : starch = 1·8 : 1.

Formula C-3 is the final result of this work on very strong glues of the starch type. Its price naturally is a little higher than that of the various starch products which make no use of acetone, but it can still be made considerably more cheaply than any other paste which is to be employed for the same purposes.

Potato starch can be substituted for cassava starch in these pastes provided the paste is to be used almost immediately. The paste made from potato starch will, in fact, be found even stickier than that made from cassava starch, but the liquefaction process is less easy and, as already pointed out on numerous occasions, the adhesives obtained with potato starch are less stable than those made from cassava starch.

Casein Glues.—Speaking generally, the casein glues possess the following advantages: High mechanical strength of the dried film; capacity for the production of films resistant to degluing due to the formation of insoluble compounds; and ease of rapid preparation by the cold process. The two principal drawbacks of the casein glues are their rather pronounced basicity (often occasioning stains) and their instability in storage beyond the shortest periods, owing to the tendency to rapid decomposition by moulds or bacteria.

Two distinct types of casein pastes are usually made: (1) The true "strong cold glues" in which the following properties are sought: Highest tensile strength together with the minimum proportion of water (to ensure rapid drying) and minimum of basicity (to avoid any tendency to stain the materials being joined). (2) Pastes for less rigorous uses in which the main object is to obtain the maximum swelling in water so as to produce a very economical glue.

The manufacture of all the casein glues is based on the property possessed by casein of dissolving in the cold in the presence of alkaline materials. In water, casein simply swells without dissolving, but with alkali solution rapidly takes place with the formation of the caseinate of whichever product is being used.

The higher the percentage of alkali used, the greater is the extent to which the casein enters into colloidal solution in the disperse phase and the more liquid is the glue produced. At the same time, increase in the quantity of alkali reduces the thickening power of the solution until the point is reached at which the whole of the casein is neutralised by the alkali.

When working with small quantities of alkali one takes the fullest possible advantage of the actual swelling power of the casein, and the pastes obtained are practically neutral. When working with higher proportions of alkali, and even with an excess of alkali over the neutralisation point, the fullest advantage is taken of the solubility behaviour of the casein, the glues produced being very strong and having a low content of water.

Casein glues are rarely made for sale at present in the liquid form, but nearly always as powders, for the following reasons :—(1) Casein solutions ferment extremely easily, particularly with a slight rise in temperature, and preservation of these solutions is difficult to secure with any certainty. The addition of chemical preservatives is invariably accompanied by a rise in production costs and greater or less alteration in the adhesive value of the solution. (2) Solubilised casein in powder form dissolves rapidly and easily in the cold, and consequently the user can make up just the quantity of adhesive solution he requires for each day's work.

For the manufacture of high-strength casein glues containing the minimum of water and alkali, yet sufficiently fluid to allow of easy spreading, it is absolutely essential to use very pure, freshly made caseins, free from fatty matter and with a low content of ash, such caseins, for instance, as are sold as "extra quality lactic caseins." The higher the ash content of the casein employed, the greater is the quantity of water required in the paste and the lower is the keeping power of the paste. The casein used should be ground fine enough to pass through a 90 or 100 sieve, so as to increase to the utmost the speed of its solution.

The following formulæ for strong wood-glue on a casein basis are worked out on the assumption that 1 kilogramme of the powder will require 2 kilogrammes of water to make the paste. This is the usual ratio. With a higher percentage of water the paste can no doubt be made less alkaline, but its speed of drying suffers. If less water

than the ratio mentioned is employed, the basicity of the paste rises to rather an undesirable value.

In practice, it is found that the sole use of a soluble alkali is not sufficient, and the usual procedure is first to mix the casein with calcium hydroxide (freshly slaked quicklime) and then to add soda ash. The soda ash reacts with the lime to form caustic soda and the latter produces the soluble sodium caseinate with the casein. After application, further reaction takes place with the formation, in the joint, of the insoluble calcium caseinate, and it is this latter slow process which is responsible for the high mechanical strength of the joint.

One thing that should never be lost sight of is that it is particularly desirable that the formula should contain the minimum quantity of ingredients which dry-out in powder form, since their presence enormously reduces the tensile strength of the casein film. The ideal formula for a high-strength casein glue which shall be neutral, have a low percentage of water and of ingredients drying-out in powder form, is still to be found, although further remarks on this subject will be made later.

In regard to preservatives, sodium fluoride is the material which offers the greatest advantages in these high-strength casein adhesives, the other merits of the fluoride in addition to its preservative effect being its influence in increasing the fluidity of the glue for a given percentage of water and in increasing the strength of the joint made. The following formula is offered as one giving an adhesive possessing the maximum of strength and the minimum of alkalinity :

FORMULA C-4.

CASEIN "STRONG WOOD-GLUE" IN POWDER FORM.

Extra lactic casein (90 sieve),	100	Mix very carefully.
Hydrated lime, . . .	18	
Soda ash, ...	5	
Sodium fluoride, . . .	7	

The various ingredients should be sieved before mixing, to produce a very homogeneous final powder.

The above powder is used as follows :—2 kilogrammes of water are placed in a receptacle—a non-metallic one for preference to avoid the formation of rust and the possibility of secondary reactions—and to this is added, whilst stirring, 1 kilogramme of powder made by Formula C-4. At first the mixture is very thick, but after from 10 to 20 minutes, according to the prevailing temperature, the mass becomes liquid, creamy and syrupy. The paste is then ready for use.

To obtain the best results from using these pastes, the following

procedure is recommended: The surfaces to be joined together are well smoothed and cleaned. The glue is coated over the two surfaces and allowed to dry for a few minutes in the air until it becomes sticky. This does not take long, since in a few minutes the glue concentrates and thickens, water being lost by absorption by the surfaces coated and by evaporation by the air. The situation is now that part of the paste is firmly lodged in the pores of the wood and the balance is on the surface. This assures the presence between the two surfaces of a layer of glue adequate to fill any small inequalities in the surfaces and to ensure a good contact, whilst the attachment is such as to ensure the glue not being forced out, and thus giving a poor joint, when the surfaces are pressed together.

The glued pieces can be worked safely after 12 to 20 hours, but it is advisable to allow them to stand for several days if the maximum tensile strength of the glue is to be obtained. The reactions which take place during this period consist of a further insolubilisation and hardening of the glue and the escape of a small quantity of imprisoned water.

Owing to its basicity, the casein glue tends to attack the brushes and these should be washed carefully after use. The powder should be kept in a well-closed metal container to avoid the alteration which casein undergoes in contact with air and moisture, particularly in the presence of lime. In winter, lukewarm water can advantageously be used to dissolve the powder.

To obtain the best results with this paste the proportions given in the formula should be meticulously observed and the water not added until the mixture has been thoroughly made. Provided it is followed exactly, the above formula, C-4, is presented as the best, the simplest and most practical casein mixture for making high-strength cold adhesives for wood.

Casein glues, with suitable modifications, can also be employed for use in the "*dry*" *gluing* method. In this method, it may be recalled, the two surfaces to be joined are coated with adhesive which is allowed to dry completely. The adhesion is then obtained by bringing the two surfaces together in a heated press under conditions which occasion the momentary softening of the glue. The interest of this process lies in allowing instantaneous gluing without the introduction of water. When working on this system, the adhesive used, whatever its type, must possess the property of reverting, even if only momentarily, under the action of the heat and the pressure, a dry glue not giving rise, it is evident, to the various colloidal phenomena associated with adhesion which take place with adhesives applied in solution.

With casein glues, dry process working may be secured by two main methods, of which the more important is the addition to the solution of sodium silicate. The sodium silicate itself reinforces, to some extent, the actual adhesive efficiency of the casein glue and forms with the lime-fluoride mixture a particularly strong product. The hygroscopic tendency of sodium silicate, occasionally a drawback, is in this instance an advantage, for the residual moisture fixed and retained by the silicate is liberated under the action of the heat; the paste becomes momentarily active and there is a definite formation of a silico-caseinate of lime which is particularly solid and resistant.

In making this type of paste Formula C-4 is again used, and after the powder has been dissolved in water, 25 to 50 per cent. of sodium silicate is added. The exact amount of silicate to be used depends upon the degree of dryness of the wood, the time of drying and that required for the juxtaposition of the treated panels (in plywood making) before pressing, and the temperature and pressure in the actual pressing operation. Each case requires a certain amount of experimentation, but this is not a difficult matter, all that is required being to make pastes with gradually increasing additions of silicate and then try them out.

The application of these pastes is simple. The panels are coated and allowed to dry. They are then cemented together by the influence of heated presses, the pressure employed being as high as desired, since there is no risk of the adhesive being squeezed out.

A casein glue made by the normal procedure, according to Formula C-4, is not suitable when the method of application is to be that modification of the dry gluing process in which two separate solutions form an insoluble adhesive mass on contact. In this case use is made of a base, such as ammonia, which forms a soluble caseinate. Ammonia is, of course, also used in connection with ordinary glue adhesives, but it is a particularly serviceable base with casein, since it increases the strength of the glue and, being volatile, eventually disappears practically completely, with the absence of any disadvantages as to hygroscopicity which may be present when using the fixed bases.

The quantity of ammonia to be used can vary from one-half of the weight of the casein to equal quantities of the two materials. The higher the proportion of ammonia employed, the greater is the initial basicity of the paste, with its resultant drawbacks, but the lower is the quantity of water that need be used to obtain a concentrated paste.

In application for plywood or other wood-joining processes, half of the wood panels are coated with the solution of soluble ammonium caseinate and put on one side to dry. The remainder of the panels

are immersed in the solution containing the insolubilising composition and, immediately prior to joining, they are withdrawn from this solution, placed in layers between the dried coated panels, and the joint made by the action of the heated press. The insolubilising solution, or rather suspension, consists esssentially of freshly made milk of lime, which decomposes the ammonium caseinate with the liberation of free ammonia and the formation of insoluble calcium caseinate. In addition, the bath contains a coagulating and supplementary insolubilising agent such as tannin or formaldehyde solution.

An alternative and technically better method, although a rather more costly one, is to use 30 per cent. formaldehyde solution as the insolubilising means. The panels, in such a case, are simply coated with this solution which, on coming into contact with the ammonium caseinate under the conditions of the fabrication process, combines with and fixes the ammonia in the form of hexamethylenetetramine, the resultant joints being exceptionally strong and extremely waterproof.

The very simple method given above for the preparation of a casein wood glue for direct application and the two methods for the dry gluing process are perfectly satisfactory for all the usual applications.

There is one point in connection with the testing of these strong wood adhesives that might be stressed here. In carrying out tensile strength tests by means of the dynamometer one frequently finds the tensile strength of the joint increased by the addition of some new ingredient to an adhesive paste. In the majority of cases, however, this apparent improvement in strength is nothing more than a reflection of a change in the viscosity of the paste in relation to the absorptive properties of the wood surface. An increased viscosity in an adhesive, for instance, is sometimes accompanied by a decrease in the quantity of adhesive absorbed by the wood. In all work on the strength of adhesives the materials should be of the same viscosity if strictly comparative results are to be obtained.

The addition of small quantities of *wetting, emulsifying or dispersing agents* facilitates the rate of solution of casein, gives the solution a greater stability whilst, particularly in the case of products to be applied by the dry gluing methods, improving the actual adhesion. The addition for this purpose of such stable colloids as gelatin and gum arabic is often advised, but actually such materials are of little value and they definitely tend to reduce the waterproofness of the glue. Products such as lecithin are being used by some makers of casein glues, but the writer's opinion is that on the balance the advantages are with using the materials mentioned below.

The emulsifying agents used are employed in very small quantities, say from 0·5 to 1·0 kilogramme per 100 kilogrammes of finished paste. The water for dissolving the casein powder may contain a little soap, or sodium sulphoricinoleate or 90 per cent. acid ammonium sulphoricinoleate with or without a little petrol may be employed, the material being dissolved in the water to be added to the casein powder. Other wetting agents which may find useful application are sodium naphthalene sulphonate or, better still, the sodium salt of butyl naphthalene sulphonic acid. They all act by facilitating solution of the casein, by increasing the homogeneity of the paste, by enhancing its adhesive power and by prolonging the period during which the paste is suitable for use. Certain organic accelerators of the vulcanisation of rubber have also been found useful in this connection.

The point must not be lost sight of, however, that the addition of wetting and emulsifying agents is, after all, only a refinement and that for the great majority of purposes there is no need to depart from Formula C-4.

Since it is essential, in any case, to use these strong casein glues as soon as possible after the preparation of the solutions, the addition of powerful antiseptics is an extra cost that is largely unwarranted, the basicity of the mixture and the presence of the sodium fluoride affording adequate protection against decomposition. It should be taken as a general working rule that, wherever possible, the only materials to be introduced into a strong casein glue are those of actual value in the solution process or which confer specific mechanical properties on the adhesive.

All the equipment used in making and handling these casein glues should be maintained in a perfect state of cleanliness for, although the freshly made casein paste preserves perfectly during its normal short period of use, contamination from dirty receptacles may mean fermentation setting in almost immediately, especially if the temperature is at all on the high side.

Quite recently, the use in casein adhesives of water-miscible organic bases of the type represented by triethanolamine or the glycol derivatives has been suggested. The writer has not yet found the time to make sufficient tests to warrant him expressing a definite opinion on the industrial value of these new materials, but their comparatively high cost and their hygroscopicity do not seem to him particularly strong points in their favour.

The manufacture of casein adhesives which have not to meet the rigorous requirements of strong wood glues and in which the ratio of water to solids is relatively high, is extremely simple. Borax is the alkali usually employed for this purpose, since it is not only a good

solvent for the casein, producing a stable solution, but it possesses marked efficiency as an antiseptic in retarding the fermentation of the solution.

FORMULA C-5.

ECONOMIC CASEIN GLUE FOR ORDINARY USES.

Lactic casein, 90 sieve, . . .	100	Mix carefully.
Borax, ...	16	

The percentage of borax used in the above formula is only sufficient to dissolve a portion of the casein, advantage being thus taken of the swelling power of the casein itself. In use, from 5 to 6 kilogrammes of water are added to each kilogramme of the powder made by the above formula. If the paste is to be used immediately, tepid water is used, but cold water can be employed when the paste is made up the evening before it is to be used. Such a paste is practically neutral. It is very economical, very tough and has remarkably good sticking powers—a characteristic of all casein glues.

When used in connection with leather, in footwear manufacture in particular, a small quantity of wetting agent should be incorporated in the water for making up the adhesive solution.

The quantity of borax used in the above formula is not sufficient to assure prolonged conservation of the paste, particularly of highly diluted pastes, the conditions in which are most favourable to the multiplication of micro-organisms. All the utensils employed in making or handling these pastes should be washed with boiling water from time to time.

Instead of borax, sodium carbonate may be used as the alkali in these ordinary casein glues as, for instance, in Formula C-6 :—

FORMULA C-6.

ECONOMIC CASEIN GLUE FOR ORDINARY USES.

Lactic casein, 90 sieve, . . .	100	Mix carefully.
Soda ash, ...	20	

For an ordinary-type casein glue which is to be as resistant to moisture as possible and yet not to meet the rigorous requirements of strong wood glues the following formula is recommended :—

FORMULA C-7.

ECONOMIC WATERPROOF CASEIN GLUE.

Lactic casein, 90 sieve, . .	100	Mix carefully.
Soda ash, ...	20	
Hydrated lime, . . .	6	

Finally, a formula is given (C-8) for the direct preparation in liquid form of a casein glue which possesses excellent water-resistance after drying. As a general rule, however, it is better to make these casein glues by the all-dry mixing process and to take up with water before using. In this particular formula the insolubilising agents are omitted, ammonia, which volatilises on the drying of the paste, being used as the main alkali.

FORMULA C-8.

LIQUID WATERPROOF CASEIN GLUE.

Casein,	12	Allow to swell.
Water,	12	
Water,	70	Add, and heat on the water-bath (maximum temperature, 60° C.), stirring until solution is complete.
Ammonia, sp. gr. 0·90,	3	
Caustic soda solution, 36° Bé.,	1·500	
Phenol,	0·500	

CHAPTER XI.

MISCELLANEOUS COLD ADHESIVES.

By the use of cold adhesives based on starch, dextrin and casein, as discussed in the three preceding chapters, the whole range of industrial adhesion problems for substances and materials possessing an affinity for water can best and most cheaply be solved. In the present section however, the various adhesive products derived from other raw materials will be dealt with.

Ordinary Gelatin Glue is universally known and supplied in the form of dry sheet, cake, etc., which is allowed to swell in water and dissolved by the application of heat on a water-bath. The only points which will be considered here will be how far a gelatin glue adhesive can be modified and made suitable for special purposes. In particular the following matters will be considered, *seriatim*:

(1) Improvement in mechanical strength.
(2) Improvement in resistance to degluing.
(3) Liquid glues produced by the acidification processes.
(4) Liquid glues produced by mixture with a non-gelatinising adhesive.
(5) Liquid glues produced by mixture with various chemical compounds.
(6) Hygroscopic liquid glues.

(1) The writer has carried out numerous trials with the object of finding methods for improving the strength of ordinary glue, the testing methods used being those described earlier in this book. A detailed account of these tests would occupy too much space, whilst they are not really germane to the scope of the present volume, which deals primarily with the cold glues.

So far as strength, as measured by resistance to tensile pull, is concerned, it must suffice to state that a good glue is sufficient in itself. The addition of other materials means not only unnecessary expense, but is often actually harmful owing to the occurrence of chemical interaction which alters to a greater or lesser degree the

collagen. In the various trials carried out, many cases were encountered where the addition to the glue of reactive chemical products, or even of inert loading materials such as zinc oxide, lithopone, barium sulphate, calcium carbonate, etc., seemed to improve the strength of the adhesive. When the tests were repeated on a sufficiently large number of samples, however, it was found very doubtful whether the apparent improvement actually did occur, the probability being that the various additions were simply correcting faulty conditions in the adhesive or in the processing. For instance, the original adhesive might have been too fluid, the wood too hot or the pressure applied during assembly of the test piece too high.

It is in their freedom from the uncertainties underlying the use of ordinary glue that the superiority of the casein adhesives really lies, especially the casein adhesives applied by the direct method as described in the preceding chapter. By the adoption of the principles of casein application to ordinary glues some of the uncertainties referred to above can be avoided. For instance, better and more reliable results are obtained by first giving the wood a preliminary coating with a dilute solution of glue. This dilute solution impregnates and blocks up the pores of the wood.

Of all the materials which the writer has investigated as possible incorporants of ordinary glue, the only one of any practical value is ammonia, a material useful in connection with all the protein-type adhesive bases. The ammonia should be employed in very small quantities, not more than 0·5 to 1 per cent. on the weight of the dried glue film.

All the agents tending to liquefy gelatin solutions in the cold tend at the same time to reduce the strength of the adhesive and to affect adversely the resistance to degluing.

The strength of the ordinary glues increases, up to a certain point, with increase in the time taken to make the joint and also with increase in the time of drying. The strength of these adhesives, as measured by the resistance of the test pieces to pulling stresses, is very often a function of the concentration of the adhesive solution.

(2) Resistance to degluing, which is of course directly related to the initial strength of the glue, is naturally also often a function of the concentration of the solution. This is why, particularly with dilute adhesive solutions, it is preferable to conduct the sticking process in two stages and with two solutions.

To increase the resistance of an ordinary glue to degluing the only practicable method is that whereby the glue is transformed into an insoluble product with the aid of such materials as formaldehyde, tannin, ammonia alum, chrome alum, potassium bichromate, acetate

of alumina, etc. From time to time suggestions have been made to add to the glue solution materials such as linseed oil, the resinates, emulsions, etc., but the net result of such additions is to decrease the strength of the joint made without influencing in the slightest degree its resistance to degluing.

There are two methods of carrying out the insolubilisation process. The first consists in coating the wood being treated with a solution of the insolubilising agent before making the joint, the wood having already received its coating of adhesive solution. If this method be used, both formaldehyde and acetate of alumina give good results. The second method, which is by far the better, is to add the insolubilising substances to the adhesive solution. Care must be taken, however, that the correct amount of the insolubilising agent be used. If too little is employed, the resistance of the joint to degluing is inadequate whatever be the time taken for drying, for at a certain stage the process of insolubilisation stops. If too much of the agent be employed, the insolubilisation and coagulation of the glue are too rapid and the adhesive becomes unusable.

When employing formaldehyde, the second process is undoubtedly to be recommended. It should be noted, though, that whilst formaldehyde is an excellent material for improving the resistance to degluing of gelatin adhesives, ammonia is the slightly better material to add when the object is to raise the strength of the glue.

About one per cent. of formaldehyde on the weight of the dry glue should be employed—not less than 0·5 per cent. in any event. It is highly advisable, also, to have present a further substance capable of slowing down somewhat the rate of the formation of the insoluble compound between glue and formaldehyde. Ammonium sulphocyanide is such a material, but acetic acid and ammonia are also useful, since in the presence of either of these latter the insolubilisation reaction is slowed up. The volatile acid or base slowly evaporates, the net result being the formation of the gelatin-formaldehyde compound at a most convenient rate from the viewpoint of the user of the adhesive.

If the joints are not to be made by the action of a hot press, the various additional substances may be used in the proportions of 1 kilogramme of formaldehyde (30 per cent. solution) to about 2 kilogrammes of ammonium sulphocyanide or about 5 kilogrammes of acetic acid. The sulphocyanide or acid should be added first to the glue solution, the formaldehyde diluted with about half its volume of water being added last.

The best and cheapest method of insolubilising ordinary glues consists, however, in the utilisation of the condensation product of

formaldehyde and ammonia known as hexamethylenetetramine or hexamine. For the purpose of the adhesives maker a solution of this product may readily be made in the following way :—

FORMULA D-1.

PREPARATION OF HEXAMETHYLENETETRAMINE.

Ammonia, sp. gr. 0·90, . .	100	Mix.
Water, ...	100	
Formaldehyde solution, 30 per cent., ...	100	

The addition of water is made with the object of minimising the effervescence and liberation of heat which occur during the reaction. After about an hour the solution is ready and should be almost neutral. Hexamethylenetetramine, as such, has no insolubilising effect on gelatin, but under the conditions of the hot press the material decomposes, liberating formaldehyde, which acts on the glue. In the presence of a small amount of dilute volatile acid, insolubilisation by hexamine can proceed in the cold, but much more slowly and too a less complete degree. About 2 to 3 per cent. of hexamine on the weight of the glue should be used.

To avoid mistakes either by premature coagulation of the glue or by an insufficient degree of insolubilisation, the reaction of the hexamine-gelatin mixture should always be tested by litmus and brought to neutrality if necessary by the addition of either dilute acid or dilute ammonia.

These adhesives find application not only on wood but also on leather (footwear, belting, etc.), and in this connection suggestions have been made for the addition to the glue solution of materials such as rosin, fats, turpentine oil and garlic oil, but the result of the use of such materials in all cases has been to lower the strength of the glue. A far more practical method of utilising the gelatin adhesives on leather is to employ the hexamine-treated product, as discussed above, with the addition of a small quantity of a wetting agent. Here again 90 per cent. acid ammonium sulphoricinoleate is the material to be preferred, being better than neutral ammonium sulphoricinoleate. The wetting agent should be employed in the proportion of about one part per thousand parts of the glue solution.

(3) A good waterproof cold adhesive of the ordinary glue class can be made by insolubilising the glue with the aid of potash alum. The compound produced, although insoluble in water, is soluble in a mixture of acetic acid and alcohol. After application of such a

solution, the solvent mixture evaporates by drying, leaving behind the insoluble alumised glue.

Formula D-2.

Waterproof Liquid Cold Glue.

Potash alum,	10	Allow to swell in the cold, heat on the water-bath for 5 to 6 hours, replacing the acid lost by evaporation.
Acetic acid,	125	
Glue,	100	
95 per cent. denatured alcohol,	125	Add to the lukewarm solution.

All the methods available for the production of liquid cold adhesives from ordinary glue by the action of acid, alkalis or salts lead in greater or lesser degree to an alteration or degradation of the collagen molecule. Both the acids and bases inhibit gelification. On prolonged contact, the bases are more far-reaching in their action than are the acids, and it is for this reason that the latter are usually preferred.

Prolonged heating favours the degradation of the collagen and loss of gelifying power and it is preferable in all cases to make these liquid glues at a moderately low rather than at a high temperature. If the amount of acid, base or salt in the solution is adequate, no supplementary addition of preservative is necessary. If a preservative is to be used, however, phenol, formic acid, benzoic acid, salicylic acid or salicylic acid in conjunction with borax are all serviceable. In most cases a little benzaldehyde is useful to prevent the growth of surface moulds.

The acid mainly used in the preparation of these cold glues is acetic acid, as olfactory inspection of most of the commercial materials sold in tubes will soon indicate. The quantity of acetic acid to be used depends on the quality of the glue, on the concentration of the solution and on the prevailing temperature. The proportion of water can be 1, 2, 3 or 4 times the weight of the glue, or even more.

The proportion of gelatinisation-inhibiting material necessary decreases as the dilution of the solution increases, whilst it is also dependent upon the quality of the glue used. The percentage to be used with any given type of liquid adhesive can rapidly be determined by a few simple trials. The glue solution is made on the water-bath and a very small quantity of the gelatinisation-retarding agent added. A small sample is then taken and put on one side for a few hours to cool and stabilise. A further small quantity of the agent is then added to the main glue solution and a further sample taken and put on one side. The sample which gives satisfactory results with the minimum quantity of protective reagent can thus easily be ascertained.

FORMULA D-3.

LIQUID COLD GLUE.

Glue,	100	Dissolve the mixture on the water-bath.
Water,	100 to 200	
Acetic acid,	75 to 100	

Instead of acetic acid, use can be made of nitric acid or oxalic acid. With these latter acids, much smaller quantities are used and the mixture is prepared with prolonged heating, the excess of acid finally being neutralised with carbonate of lime.

FORMULA D-4.

LIQUID COLD GLUE.

Glue,	100	Heat on the water-bath for 4 to 5 hours.
Water,	300	
Oxalic acid,	8	
Calcium carbonate,	Quant. suff.	Determine neutralisation point with litmus.

(4) By mixing glue with an adhesive which does not gelatinise, there can be obtained an excellent very adhesive neutral glue which does not set. As the non-gelatinising adhesive gum arabic or, better still, dextrin, is suitable. Dextrin alone produces very concentrated and fluid solutions, but they are rather lacking in viscosity and give a dried film which is rather too brittle and too crystalline. Glue solutions alone give a very pliable film, their disadvantages being their tendency to gelatinise when concentrated and too high a viscosity. Glue and dextrin are thus largely complementary, particularly as glue solutions constitute excellent agents for the suspension and stabilisation of dextrin solutions.

In the same order of ideas, small quantities of glue can be added to solutions of dextrin or gum arabic to increase their viscosity and to allow of the augmentation of their water content.

(5) Another method for obtaining liquid glues depends upon the action of certain chemical products. Quite a range of such products is available, but mention may be made particularly of carbolic acid, resorcinol, chloral hydrate, zinc chloride, caustic soda and caustic potash. Three formulæ only for this type of liquid glue will be given. They are all practical and they are all of interest to the manufacturer of liquid glues put up in tube form.

By heating ordinary glue with 50 per cent. of its weight of hydrated lime, a liquid glue can be obtained, but at the expense of a deep-seated alteration in the character of the collagen, this change continuing

after the glue has been made. A better way of carrying out this process is to use the lime in the form of sucrate of lime :—

FORMULA D-5.

LIQUID GLUE MADE WITH LIME SUCRATE.

Water,	100	Heat for 8 hours at 80° C.
Hydrated lime,	3	
Sugar,	35	
Glue swollen by immersion in its own weight of water,	200	Add, and boil for 2-3 hours, replacing the water lost by evaporation.
Carbolic acid,	0·100	Add and mix.
Acetic acid,	0·700	

Ammonium sulphocyanide also gives very good results :—

FORMULA D-6.

LIQUID GLUE MADE WITH AMMONIUM SULPHOCYANIDE.

Water,	200	Mix in the cold, allow to swell for 24 hours and then heat for 6 to 8 hours.
Glue,	100	
Ammonium sulphocyanide,	5	

The best method, however, is that making use of sodium naphthalene sulphonate. This gives a cold glue which is perfectly liquid, very adhesive, odourless, non-acid, non-hygroscopic and which dries quickly. Sodium naphthalene sulphonate is itself only slightly soluble in water, but forms a water-soluble complex with the glue.

FORMULA D-7.

LIQUID GLUE MADE WITH SODIUM NAPHTHALENE SULPHONATE.

Glue,	100	Allow the mixture to swell for 24 hours in the cold, then heat until solution is complete.
Water,	150	
Sodium naphthalene sulphonate,	25	

This glue can be used as such, or after drying and powdering. A little methylated spirit may also be added to increase the fluidity and the speed of drying of the glue.

(6) The demand sometimes occurs for a liquid cold glue which, whilst pliable and very plastic, shall also retain a degree of stickiness. Such a product can readily be obtained by dissolving glue in water together with its own weight of a chloride, calcium chloride for preference.

FORMULA D-8.

PLASTIC LIQUID GLUE.

Glue,	100	Allow to swell for 24 hours, and dissolve on the water-bath.
Water,	300	
Calcium chloride,	100	

If the product is to be very clear and transparent, a colourless or very pale grade of glue should be used and the percentage of water increased. Part of the water should be used for dissolving the calcium chloride separately and the solution of the chloride filtered before addition to the glue. By varying the proportions and the nature of the chlorides used, and by the addition of certain other complementary products, liquid glues somewhat less plastic and less hygroscopic than the above can be obtained, representative formulæ of this type being D-9 and D-10.

FORMULA D-9.

LIQUID COLD GLUE.

Glue,	100	Swell the glue in the water, dissolve on the water-bath; add the chloride, allow to settle.
Water,	250	
Common salt,	100	

FORMULA D-10.

LIQUID COLD GLUE.

Glue,	100	Swell the glue in the water; dissolve on the water-bath.
Water,	300	
Calcium nitrate,	20	Add.
Magnesium chloride,	15	
Dinitrobenzene,	1	

Excellent cheap and very adhesive cold glues can also be made by mixing sulphite lyes (a by-product of the manufacture of paper pulp by the sulphite process) with glue :—

FORMULA D-11.

LIQUID COLD GLUE.

Water,	150	Dissolve the chloride in the cold water, add the glue, and allow to swell for 12 hours; dissolve on the water-bath.
Calcium chloride,	30	
Glue,	100	
Formic acid,	5	Add to the lukewarm glue.
Sulphite cellulose lye, 35° Bé.,	25	

To make a substitute for Vienna glue a similar type of combination is used, with the addition of inert material to increase the content of dry material and to assure a better filling :—

Formula D-12.

Cold Glue Substitute for Vienna Glue.

Water,	40	Dissolve the chloride in the cold water, allow the glue to swell for 12 hours; dissolve on the water-bath.
Calcium chloride,	30	
Glue,	100	
Yellow ochre,	2·5	Make into a paste and add.
Mineral white,	18	
Water,	10	

The glycerin-gelatin mixtures which are the basis of the copying pastes for duplicating work might also be mentioned here. The glycerin gives an elastic mass which does not harden and which facilitates the penetration of the copying ink. Owing to the high percentage of glycerin used in the mixture, the preparation will keep indefinitely without the need for further addition of antiseptic agents.

Formula D-13.

Polycopying Paste.

Gelatin,	100	Dissolve.
Glycerin,	400 to 500	

The actual amount of glycerin to be added depends on the quality of the gelatin used. If too little glycerin be employed, the number of copies obtainable is too low. With too much glycerin the paste is sticky and the reproduction blurred.

Fish glue is the best raw material of all for the manufacture of cold glues to be marketed in tubes. The fish glue is dissolved in water and its adhesive properties, remarkable enough by themselves, are further enhanced by the addition of small amounts of hydrochloric acid, tartaric acid, acetic acid, benzoic acid, etc.

Formula D-14.

Very Adhesive Fish Glue.

Pale, thick fish glue,	100	Heat on the water-bath.
Water,	10	
Benzoic acid,	0·220	Add to the tepid glue solution after withdrawal from the water-bath.
Industrial methylated spirits,	0·750	
Sassafras oil,	0·150	—Add.
Boiling water,	8	—Add.

The water-resistance of this type of cold glue can be increased and its adherence further enhanced by the addition of a saturated alcoholic solution of a soft gum resin, such as rosin, ester gum, gum lac, sandarac, kauri or pontianac. The gum is brought into solution by treating from 300 to 400 grammes with a litre of methylated spirits, solution being aided by stirring from time to time. After settling, the clear supernatant solution is withdrawn and used in the preparation of the cold glue. The undissolved gum residue is treated, after the addition of fresh gum, with a fresh quantity of alcohol. If the saturated solution of resin in alcohol were added as such to the fish glue solution, the gum would be partially precipitated owing to the dilution of the alcohol by the water. To avoid such precipitation the gum solution is treated with about a third of its volume of the fresh alcohol before addition to the glue.

Formula D-15.

Waterproof Fish Glue.

Pale, thick fish glue, . .	100	Heat on the water-bath.
Water, ...	10	
Alcoholic solution of gum resin,	100	Add to the tepid glue solution.
Industrial methylated spirits,	35	

The actual quantity of resinous solution used depends upon the viscosity desired in the finished cold glue. This type of waterproof fish glue is used for setting jewellery and particularly for affixing precious stones, etc., to glass, metals, etc.

Albumin is soluble in water, particularly in the presence of a base such as ammonia. When heated towards 80-85° C. it coagulates and becomes insoluble, this being the principle of the adhesive action of the material. Lime hardens albumin and forms insoluble compounds, especially if the materials are heated towards 100° C. Since, however, lime also tends to gelatinise the albumin, the base must not be present in excess if the keeping qualities of the preparation are to be satisfactory.

In general, the albumin adhesives behave rather like the casein glues, particularly in regard to keeping qualities.[1] As the source of the albumin, blood may be used, if it is employed perfectly fresh, but in practice albumin dried in thin leaf form is almost exclusively employed.

In the manufacture of the albumin cold glues, the raw material is first soaked for about two hours at 25-30° C. in part of the water

called for by the formula. The solution is well stirred, allowed to settle and then strained through a fine sieve to separate the insoluble matter. The ammonia is added, and then the lime diluted with the balance of the water. These additions are made slowly and the stirring should be gentle to keep down as far as possible the production of foam.

FORMULA D-16.

INSOLUBLE ALBUMIN COLD GLUE.

Water,	175	Soak for 2 hours at 25°-30° C., stir and filter.
Albumin,	100	
Ammonia,	4·2	—Add slowly.
Lime,	2	Add slowly.
Water,	25	

The glue so prepared can be used up to half a day after making. The surfaces to be joined are coated, brought into juxtaposition and rapidly pressed together in the cold before the albumin has time to coagulate. When working on wood panels, pressures of 4 to 5 kilogrammes per square centimetre (atmospheres) and a temperature of 90° to 95° C. give good results.

Albumin glues are, however, but little used to-day. They have no real advantages over the casein glues, which are more practical and cheaper. A caseinate of lime, which is itself insoluble, when treated with formaldehyde solution and heated gives a film of properties satisfactory enough for all purposes.

The use of **gum arabic** as an adhesive is universally known. By simple solution of the gum in cold water a paste can be obtained which is pale in colour, concentrated, quick-drying, very sticky, spreads easily, and is stable over prolonged periods of storage. It is exceptionally serviceable for application to paper and particularly in office pastes.

For industrial adhesives gum arabic is not so important and has little advantage to offer over the starch and dextrin products. The latter are usually cheaper than gum arabic pastes and can be made in a much wider range of concentrations and viscosities.

Although gum arabic is quite a good adhesive by itself, its properties in this respect can be enhanced by the addition of certain salts such as nitrate of lime, sulphate of alumina, etc.

To avoid the too-rapid hardening of the solution round the necks of the bottles in which it is kept, and also to mitigate the somewhat brittle nature of the dried film of gum arabic, it is usual to add some 8 to 10 per cent. of glycerin to the solution. Too much glycerin should

be avoided, as it imparts hygroscopicity to the solution and retards the rate of drying.

The ratio of water to dry gum should be from 2 : 1 to 3 : 1, depending upon the actual quality of the gum. The quantity of water may be increased, and the cost of the solution correspondingly reduced, by the addition of an agent capable of increasing the viscosity of the solution. This agent may be a gelatinising material, such as a very pale gelatin, in which case the solution must be heated to dissolve the gelatin. It may be a natural gum, such as gum tragacanth, which possesses very marked swelling properties, or it may be a synthetic material, such as the monomethylcellulose made by the I. G. Farbenindustrie A.G. under the trade name " Tylose."

In the latter two cases the mixture should be homogenised by very energetic agitation, best effected in an emulsifier or by passage through a colloid mill.

In comparison with most other adhesives, gum arabic solutions are little prone to fermentation and consequently the choice of protective antiseptics is not an onerous one, sodium chloride or, better still, lime being quite satisfactory.

Formula D-17.

Ordinary Gum Arabic Paste.

Water,	250	Dissolve in the cold, stirring from time to time. Allow to settle and filter the clear top liquor.
Hydrated lime,	0·2	
Glycerin,	8	
Gum arabic,	100	

In the chapter on Raw Materials, two different methods for the utilisation of **rosin** in adhesives were mentioned. The first was the employment of the rosin in non-aqueous adhesive solutions, the reason for the addition of the rosin in this case being principally its low price. The second was the production of water-miscible rosin adhesives obtained by the partial or total saponification of the rosin by bases.

It is this second method which will now be considered in some detail, as it is by far the more interesting and the more important. The adhesives obtained are of excellent quality, particularly for use on paper. They are very sticky and dry quickly because they are very concentrated, and they are cheap.

In the form of rosin size, the alkali resinate solutions are extensively employed, of course, in the actual manufacture of paper, but the employment of these solutions for general adhesive purposes seems to have attracted surprisingly little attention, and yet these solutions have some decidedly interesting applications.

The alkali resinate solutions can be used as such, or they can be employed to amplify the adhesive and sticky properties of glues made from other raw materials. Their influence on these other products is not confined to the two points just noted, for the alkali resinates not only increase the density and speed of drying of the adhesives to which they are added, but they impart to them a more pronounced ropy character and a better stability.

In particular, alkali resinate solutions can very advantageously be added to all the starch adhesives discussed in Chapter VIII with the exception of those materials which contain chlorides. Although these starch adhesive products are perfectly satisfactory by themselves, it is obvious that the further addition of a very adhesive and very dense ingredient cannot be other than an improvement in pastes for ordinary purposes. It should be stressed, though, that alkali resinate solutions should not be added to those starch adhesives formulated with the object of producing high-strength joints as resistant as possible to degluing. The dried resinate film is always friable, whilst the presence in it of the saponified and soluble fraction of the rosin also influences adversely the strength of the joint and its resistance to degluing influences.

The actual manufacture of rosin adhesives presents few difficulties. The few necessary guiding principles on the subject are given below, but the adhesives maker will soon have confidence enough to modify his formulæ with the object of producing materials to meet exactly his own special needs.

The principal constituent of rosin is abietic acid. French rosin also contains pimaric acid, which has an acid value somewhat higher than has abietic acid. For the purposes of the adhesives maker, the average acid value of rosin can safely be taken as 155, which means that 15·5 kilogrammes of anhydrous soda ash will be required for the exact neutralisation of the acids contained in 100 kilogrammes of rosin.

Rosin softens at about 75° C. and melts at about 120°-135° C. It is soluble in caustic soda, sodium carbonate, sodium silicate, caustic potash, potassium carbonate, potassium silicate, and ammonia.

The basic principle of the production of rosin solutions is the following: The rosin is heated in a dilute alkali solution at a temperature equal to, or rather higher than, its fusion point. The rosin is thus saponified and becomes soluble in water.

If the quantity of soda used is such as completely neutralises the whole of the acidity of the rosin used there is obtained a brown gelatinous mass of saponified rosin glue completely soluble in water. If a smaller quantity of alkali be used, only part of the rosin acids will

be neutralised, and consequently solubilised, and the material obtained will really be an emulsion, the unchanged particles of rosin being maintained in colloidal suspension by the aid of the solution of the solubilised portion of the rosin. This emulsion is very stable, possesses greater adhesive powers than a solution of wholly neutralised rosin, whilst its limpidity and colour are the better the paler the grade of the rosin used in its preparation.

Rosin is marketed in bulk, fused and solidified, in casks each containing about 400 kilogrammes gross for net. The quality to be used in adhesives making depends entirely on the price and grade of the adhesive solution to be made. Wherever price permits, it is advisable to use the paler grades. The casks should be stored as received and in a cool place. If the rosin is powdered and not used for some time it tends to lump together again and is then not very easy to handle. Further, owing to the much greater extent of surface exposed in the powdered product, oxidation will have occurred, this being reflected in the quantity of alkali-insoluble matter which is found in the material.

In practice, caustic soda or, better still, soda ash, or a mixture of the two, is the only alkali used for making resinate solutions for adhesive purposes. Caustic soda is not an easy product to manipulate. As it is very hygroscopic, once the containing drums are opened it takes up water from the atmosphere and also absorbs carbon dioxide, both of which reduce its actual alkali content. Its use, however, does mean greater rapidity in the manufacture of the sodium resinate solution than with sodium carbonate, although the principal advantage of the use of the caustic lies in the absence of froth during neutralisation.

Sodium carbonate in the form of soda ash (or soda crystals) is much easier to handle. It can be stored indefinitely if kept in a dry place. When used for the neutralisation of rosin, however, carbon dioxide gas is liberated and this produces an abundant froth.

The quantity of water used in the process depends both on the consistence desired in the finished adhesive and also on the free rosin content of the latter. When making a completely saponified rosin the actual quantity of water employed is immaterial, since the sodium resinate formed is extremely soluble, the only drawback following on the use of too great an amount of water being that the solution may not be viscous, and consequently adhesive, enough. When, however, emulsion containing free rosin is being made, the quantity of water used should, as a general rule, decrease as the quantity of free rosin increases. What takes place is that part of the properties of the sodium resinate which, in normal solution, would show themselves in the form of viscosity and concentration, are expended in

keeping the free rosin in stable suspension. If the dilution of the suspension be too high, there is the possibility that the sodium resinate will be of inadequate concentration, that equilibrium will be destroyed and that the free rosin will be precipitated in lump form.

Solutions of sodium resinate containing up to 40 to 45 per cent. of free rosin in suspension can be prepared, but these high percentages are not of interest to the adhesives maker since, even if the suspensions were able to stand storage and transport without the emulsion breaking, they would require to be diluted by the ultimate user and this dilution would lead to the liberation of droplets of free rosin and their subsequent coalescence and precipitation. This risk is reduced, of course, if the concentrated suspension of free rosin in sodium resinate is added to a solution of another adhesive, such as the starch products, for in this case the quantity of protective colloids present would be markedly increased.

As a general rule it may be taken that in the preparation of resinate adhesives the quantity of free rosin should not be more than 10 to 15 per cent. of the total rosin, and that about 14 kilogrammes of sodium carbonate should be used for the treatment of 100 kilogrammes of rosin. As a general rule, also, it is preferable to use as low a quantity of water as possible, with the object of avoiding too great a diminution of the degree of alkalinity of the solution.

A factor which places a bottom limit on the quantity of water, however, is that too thick a paste is both difficult to mix and to apply when made.

If the resinate adhesives are made in open pans, allowance should be made for the quantity of water lost in process by evaporation and entrainment in the carbon dioxide foam. This loss will vary with the duration of the operation, the temperature and the quantity of soda used. If a figure for general guidance may be given, it is that the quantity of water in the resinate suspension should be between 80 and 100 per cent. of the weight of rosin used; but it is simple to make small-scale trials on the point.

In the actual manufacture of these alkali-rosin adhesives there are two principal methods of effecting the heating stage, namely, in an open pan or under pressure in an autoclave. When making occasional and very small quantities, use can just as well be made of any convenient receptacle to hand, but when these adhesives are to be manufactured regularly it is worth while giving some consideration to the choice of heating plant.

If the open pan method is to be used, heating by the free flame, for instance by a fire underneath the pot is definitely undesirable. Not only does this method make impracticable the degree of tempera-

ture control which is necessary, but there are serious risks of fire from the frothing-over of the charge, even in those cases where an inflammable volatile solvent is not an ingredient of the solution. An alternative method is heating by the direct blowing-in of steam, but this method has the disadvantage of diluting the solution—by the condensed steam—to an undesired high degree, whilst accumulations of coagulated free rosin are likely to form and block up the pipe lines.

The best method in open pan practice is undoubtedly to use a steam-jacketed pan, preferentially a pan jacketed at its bottom only, for the cooler the side-walls remain the more speedily will the finished mass cool down and the more rapidly will the carbon dioxide froth produced subside. The size of the pan should be such that its capacity is from five to six times that of the volume of mixture being heated. With a pan of this size the dangers of the mass frothing over are minimised.

The simplest method of controlling the frothing lies in fitting at the top of the pan and just inside the walls one or two turns of piping through which cold water can be made to flow.

If the projected scale of manufacture of these rosin adhesives is sufficiently great to warrant the design and installation of special plant, then the autoclave or pressure plant makes a very strong claim. This type of plant can be heated either by an internal closed steam coil or by a steam jacket, and is fitted with a thermometer, pressure gauge, safety valve and agitator. By working under autoclave conditions, the frothing difficulty and losses due to evaporation are both completely obviated, whilst the size of the plant for a given output is considerably less than with the open pan. Further, whilst when working in the open pan the time required to complete a batch of average size may be taken as 8 to 9 hours, under autoclave conditions the time necessary is reduced to 4 to 5 hours, since both saponification and emulsification take place more rapidly when working at temperatures higher than the melting-point of the rosin.

For the actual making of the batch three different methods are possible: First the addition of the rosin to the soda; secondly the addition of the soda to the rosin; and thirdly the addition of powdered rosin to a solution of completely saponified rosin.

In the first method the solution of alkali in water is put into the pan and heated to about 130° to 140° C., that is, to a temperature just a little higher than the fusion point of the rosin. The rosin, which has been powdered immediately prior to its use, is then added to the alkali in small quantities at a time, the temperature of the solution being maintained. If the temperature of the batch is allowed to fall below 130° C. either by inadequate heating or by the introduction

of too large quantities of the cold rosin at a time, the rosin does not immediately melt, but agglomerates into lumps which prove most difficult to bring into solution. If the temperature is allowed to rise above 140° C. the great danger is that of frothing-over (when working with sodium carbonate in an open pan) owing to the rapid liberation of large volumes of carbon dioxide gas.

In the second modification of working method, the rosin in lump form is put into the pan and melted, using a temperature just higher than the melting-point of the rosin. The alkali solution, heated to the same temperature in another pan, is then slowly added. Since the two reactants meet at similar temperatures and both are in the liquid condition, saponification takes place almost instantaneously, all that is necessary being to maintain the temperature by the application of slight heat. This process is preferable to the one first described, and is the more rational. It does away with the necessity for the preliminary powdering of the rosin, the saponification is more regular and more rapid, whilst any incipient troublesome frothing can be more easily controlled by the temporary stopping of the addition of the alkali.

The third of the processes referred to is not of any great practical interest. It consists in preparing a completely saponified rosin by either of the two first-mentioned methods, but using such a quantity of soda that the whole of the rosin is saponified, the final solution being slightly on the alkaline side. Rosin in powdered form is then added and dispersed in the sodium resinate solution, the temperature being maintained and agitation being vigorous until emulsification is complete.

For open pan working the second method is undoubtedly the best of the three, the quantity of soda used being adjusted to leave the desired proportion of free rosin in the solution.

The actual saponification and emulsification stages can be taken as requiring about 5 to 6 hours, but heating and mixing should be continued for a further two hours or so to make sure of the absence of free alkali and the production of an emulsion which will show no tendency to break on dilution prior to use.

Working under autoclave conditions the technique of the process is still simpler. The rosin, in large lumps, is introduced into the pressure vessel through the manhole and is followed by the soda solution. The autoclave is then closed, the safety valve set to blow off at a pressure of three and a half atmospheres and the vessel heated to 130° C. for two hours by means of its steam-jacketed bottom. During this stage the agitator is not in action, but after the two hours it is run for about a minute. The agitator can be of simple paddle

type actuated by a hand wheel outside the autoclave. Under the influence of the stirring the pressure mounts in the autoclave due to the liberation of carbon dioxide, and the surplus gas escapes through the safety valve. If the agitation has been gentle, and not prolonged for more than a minute, there is little risk of any of the solution passing out through the valve with the carbon dioxide. After a further fifteen minutes of heating, the agitator is used for a further minute and more gas escapes. This sequence of operations is repeated over a period of two hours, the whole process under autoclave conditions thus taking about four hours. Working by this method the production of resinates containing very high amounts of free rosin in suspension is possible.

Whatever the process used, a sample taken when the batch is finished should remain perfectly clear and limpid on cooling. Further, 1 gramme of the solution shaken with 50 c.c. of boiling water should give an opalescent homogeneous solution. If these results are not obtained the batch is not finished and the heating should be continued.

In regard to actual quantities, the following formulæ are given as working bases :—

FORMULA D-18.

SODIUM RESINATE ADHESIVE.

Rosin,	100	Work by the methods described.
Water,	80	
Soda ash,	15	

By the addition of a little caustic soda, solution can be facilitated, as in the following formula :—

FORMULA D-19.

SODIUM RESINATE ADHESIVE.

Rosin,	100	Work by the methods described.
Water,	80	
Caustic soda,	1	
Soda ash,	13·7	

With caustic soda as the sole alkali, the following formula is given :—

FORMULA D-20.

SODIUM RESINATE ADHESIVE.

Rosin,	100	Work by the methods described.
Water,	80	
Caustic soda,	11·25	

The quantities of caustic soda in Formulæ D-19 and D-20 refer to solid caustic. If lyes are employed, a corresponding reduction should

be made in the quantity of water used in the batch. If it is essential to use an open pan, then caustic does offer advantage as the saponifying agent, particularly when the alkali solution is added to the fused rosin, as in the second of the open pan methods described above.

The concentrated resinate products should be protected against low temperatures during storage; otherwise the colloidal equilibrium is likely to be broken and rosin precipitated, particularly from products rich in free rosin. As noted earlier, completely saponified rosins can be diluted without any difficulty. With products containing free rosin dilution is best effected with warm water and vigorous stirring. The dilution can be conducted, if necessary, in the pan in which the resinate has been made. The use of soft water, for instance condenser water, is in all cases preferable, for when diluted with hard waters the solution is likely to be turbid, especially with resinates containing substantial amounts of free rosin.

A content of free rosin of 15 per cent. on the weight of the batch may be taken as the limit above which it is unsafe to go if the material is to be diluted with water alone.

Coumarone has been suggested as a partial substitute for rosin in this type of adhesive. Its price, however, is against it whilst, as it cannot be saponified, it can only be used to replace the free rosin as the disperse phase of an emulsion in which sodium resinate solution is the continuous phase. Further, the addition of coumarone introduces mechanical complications, so that on the whole it can be dismissed as of little practical interest.

Lime itself is only very slightly soluble in water, but on boiling with solutions of sugar (cane or beet) it forms **calcium sucrate** or saccharate, a compound which is fairly soluble and which has adhesive properties distinctly higher than the poor ones possessed by sugar solutions alone. Up to 40 grammes of lime can be dissolved in a litre of water containing 40 grammes of sugar. A representative formula for making such a solution is the following:—

FORMULA D-21.

LIME SUCRATE ADHESIVE.

Water,	250	Dissolve.
Sugar,	100	
Water,	50	Add and heat at 80° C. for 8 hours.
Hydrated lime,	25	

Sucrate of lime is rarely used alone as an adhesive but is occasionally employed in admixture with ordinary glue, fish glue or gum arabic adhesives.

The **waste sulphite lyes** resulting from the manufacture of wood pulp for the paper industry by means of the sulphite process can also be used as the basis of industrial cold adhesives. The material has the advantages of cheapness and of producing flexible dried films, but its drawbacks include its acidity, rather dark colour, hygroscopicity and comparatively poor adhesive efficiency. The crude dark brown sulphite waste lyes are better adhesives than the paler grades that have been subjected to a partial purification process. No matter what method of refining be used, whether treatment with sodium hydrosulphite, oxidation by blowing in hot air or otherwise, there is always marked prejudicial alteration of the adhesive properties of the lyes.

From the viewpoint of the user of sulphite lyes for adhesive purposes probably the least harmful method of partial purification is that dependent upon neutralisation with milk of lime. Unfortunately, the lime renders the dried film rather friable, but trials carried out by the writer have shown that this drawback can be partly rectified by the addition to the lime of calcined magnesia. Further, the addition to the sulphite lyes of formaldehyde in the proportion of 3 to 5 per cent. improves the adhesive value and has a beneficial effect on resistance to degluing.

The most rational viewpoint the adhesives maker can adopt in regard to sulphite lyes, however, is to envisage the material simply as a very cheap product which can be made into workable adhesives by the addition of true glues such as hide glue, casein, etc. The writer again suggests, however, that in view of the almost universal applicability of the adhesives made from the starches and modified starches, the employment of materials such as sulphite lyes is not in general circumstances worth worrying about a great deal. The following formulæ can be used, if desired.

Formula D-22.

Sulphite Lye Adhesive.

Sulphite lye, 33° Bé.,		100	Heat for 1 hour whilst stirring.
Hydrated lime,	11		
Water,	80	91	

Formula D-23.

Improved Sulphite Lye Adhesive.

Sulphite lye, 33° Bé.,		100	Neutralise the lye with the lime, add the magnesia, mix for 1 hour.
Hydrated lime,	2		
Water,	20	22	
Calcined magnesia,		9	

Since sulphite lye is a decidedly variable product, the final material should always be tested with litmus and corrected to neutrality, where necessary, by the addition of either further sulphite lye or of lime.

Formula D-24.

Cheap Casein-Sulphite Lye Adhesive.

Sulphite lye, 33° Bé.,		100	Mix and correct, if necessary, to assure neutrality.
Hydrated lime,	2		
Water,	20	22	
Lukewarm water,		70	Add the solids successively to the tepid water. When dissolved mix with the first solution.
Sodium carbonate,		2	
Hydrated lime,		0·6	
Casein,		10	

Formula D-25.

Sulphite Lye-Glue Adhesive.

Sulphite lye, 33° Bé.,	100	Mix well whilst boiling the solution.
Lead acetate,	5·3	
Glue (ordinary),	10	
Hot water,	10	

Formula D-26.

Rubber-like Sulphite Lye Adhesive.

Sulphite lye, 33° Bé.,	100	Heat slowly to 80° C. over a period of 20 minutes.
"Durolin" (I.G. Farb. A.G.),	3	
Formic acid, 80 per cent.,	1·5	

Formula D-27.

Liquid Gluten Substitute.

Calcium chloride,	30	Allow the glue to swell, and dissolve on the water-bath.
Water,	100	
Glue,	100	
Kaolin,	120	Add and mix.
Sulphite lye, 33° Bé.,	100	
Benzaldehyde,	0·2	

Formula D-28.

Vienna Glue Substitute.

Sulphite lye, 33° Bé.,	100	Heat the lye and add the kaolin and glue whilst stirring.
Kaolin,	50	
Water-swollen glue,	20	

Sodium silicate is a material possessing excellent adhesive properties, whilst it has the added advantages of cheapness and rapidity of drying. Its principal drawback is its pronounced alkalinity,

which rules out its employment in a number of instances. Its use in admixture with other adhesives either as such or in the form of silica gel has already been discussed.

Trials have been made on numerous occasions as to the possibilities as industrial adhesives of solutions of sodium silicate to which have been added other mineral compounds such as borax, sulphate of alumina, zinc chloride, magnesium chloride, etc., but the results obtained have not been of any great interest.

In the writer's experience the best solution of the problem of utilising to the full the adhesive and rapid-drying action of sodium silicate in simple adhesives, and at the same time minimising its free alkalinity and tendency to spot and stain, is to employ it in conjunction with rosin as a substitute for the caustic soda. The silicated rosin adhesives so obtained are of high density and are rapid-drying.

The principal difficulty in carrying out this process is to avoid the precipitation of the silicate by the rosin acids, with the formation of clots of silica gel and unconverted free rosin. This danger can be minimised by working in the cold and adding the rosin to the silicate in as finely divided a condition as possible. It is further advisable not to carry the reaction to completion, but to work with the proportions of about 5 kilogrammes of rosin to 100 kilogrammes of 36° Bé. sodium silicate solution. If this proportion be exceeded, part of the silicate will be precipitated as silica gel around the particles of which free rosin adheres. This undesired course of the reaction becomes the more prominent as the ratio of rosin to silicate increases above the figures quoted, until finally the stage is reached at which the adhesive sets to a solid block.

Formula D-29.

Silicated Resinate Adhesive.

Sodium silicate solution, 36° Bé.,	100	Mix.
Powdered rosin, . . .	5	

The mass is introduced into a mixing pan provided with a powerful agitator and agitation continued until perfect solution is obtained. The product is a pale transparent solution, more viscous, more adhesive and quicker-drying than silicate alone and with the further advantage of a considerably lower content of free alkali.

The subject of sodium silicate adhesives, however, is more fully dealt with by Dr. W. S. Macfarlane, of Imperial Chemical Industries, in the next chapter.

CHAPTER XII.

SODIUM SILICATE ADHESIVES.

(*By* W. S. MACFARLANE, B.Sc., Ph.D.)

SODIUM silicate (silicate of soda) is the only inorganic material extensively used as an adhesive, for which purpose it is especially suited by reason of its low cost, high strength and rapid set. The name " sodium silicate " does not represent a single chemical compound, but is applied to all combinations of sodium oxide and silica, and also to all solutions of such combinations in water.

By no means all forms of sodium silicate can be used as adhesives, and those which can be so used vary considerably in viscosity, rate of drying, density and other properties which are important in the choice of the correct adhesive for a particular type of work. It is therefore necessary to consider in some detail the different varieties of sodium silicate.

Sodium silicate in the form of the solid glass is made by fusing a mixture of sand (silica) and sodium carbonate (soda ash). During the fusion the sodium carbonate is decomposed by the silica with formation of sodium silicate and evolution of carbon dioxide. The process is very similar to the manufacture of ordinary glass, the essential difference being the omission, in sodium silicate manufacture, of the calcium carbonate (limestone) which confers the property of insolubility on ordinary glass. The sodium silicate obtained is a transparent, very hard and brittle material resembling ordinary glass. The composition of this glass depends upon the proportions of silica and sodium carbonate in the mixture before fusion. Ordinary commercial soluble glasses vary in composition from a glass consisting approximately of two parts of silica combined with one part of sodium oxide, to a glass consisting approximately of four parts of silica combined with one part of sodium oxide. These are referred to as having molecular or weight ratios of 2 : 1 and 4 : 1 respectively. By

a coincidence "molecular ratio" and "weight ratio" are nearly identical in the case of sodium silicate. For present purposes it is not necessary to consider this distinction further, but references in the following pages to "ratio" means molecular ratio of silica to soda.

Sodium silicate glasses differ from ordinary glass in being soluble in water. They are not, however, readily soluble in water; even when finely powdered they dissolve only slowly in hot water and very slowly in cold water. Moreover, the dissolution of the glass does not proceed uniformly, as the sodium oxide dissolves much more readily than the silica, so that the resulting solution may be of very different ratio from the glass. For those reasons the glass is usually dissolved by the manufacturers, who have special facilities for carrying out the process and for controlling the composition of the resulting solutions. The solutions thus obtained are each sold as having a definite composition (*i.e.*, ratio of silica to sodium oxide) and a definite concentration or strength (usually measured by the density of the solution). Two solutions may have the same ratio but different densities and such solutions will have quite different adhesive properties. Again, two solutions may have the same concentration but different ratios, and such solutions will also have quite different adhesive properties. It is therefore necessary to consider the relationships between the concentration and composition of sodium silicate solutions and their adhesive properties.

Composition.—The composition of the types of sodium silicate used as adhesives varies, as already stated, between the limits of two and four parts of silica to one part of sodium oxide. No definite chemical compounds are known between these limits and the substances having a higher ratio than 2 : 1 may be regarded as solutions of silica in sodium disilicate (a chemical compound having the ratio 2 : 1). The silica in solutions of ratio 2 : 1 and over is partly in true solution and partly in colloidal solution. The proportion of silica which is present as a colloid rapidly rises as the concentration of the solution is increased; concentrated solutions therefore exhibit the characteristic properties of a colloid or glue.

Concentration.—Sodium silicates of ratio 2 : 1 or higher have no definite maximum solubility. A dilute solution may be concentrated and will gradually increase in density, passing from a mobile liquid through the stages of a thick syrup and a jelly to, eventually, a glass. A practical limit to the concentration of these solutions is fixed, however, by the condition that they must remain fluids that can be handled by the ordinary methods applicable to fluids, such as pouring, pumping, etc. The majority of the sodium silicate solutions of

commerce are supplied at or near this practical limit of concentration.

The following table shows how the practical limiting concentration varies with the ratio of the sodium silicate :—

Ratio SiO_2/Na_2O	Per cent. Sodium Silicate	Density		
		Specific Gravity	Degrees Twaddell	Degrees Baumé
2·0 : 1 . .	55	1·70	140	60
2·5 : 1 . .	47	1·56	112	52
2·9 : 1 . .	45	1·50	100	48
3·3 : 1 . .	40	1·42	84	43
3·95 : 1 . .	33	1·30	60	33

It will be seen that sodium silicate of ratio 2 : 1 can be made as concentrated as 55 per cent. and that the maximum concentration decreases continuously as the ratio of the sodium silicate is raised; sodium silicate of ratio 3·95 : 1 is not available at concentrations greater than 33 per cent.

Viscosity.—Viscosity is the most important physical property of sodium silicate solutions in their application as adhesives. The viscosity of such solutions of any ratio increases as the concentration or density rises. The rates of increase of viscosity with concentration are, however, very different for silicates of different ratios. This difference may best be illustrated by examples.

Sodium silicate solutions of ratio 2 : 1 have a very low viscosity (not greatly different from that of any dilute salt solution) if the density is below about 80° Tw. As the density of the solution increases above this point, the viscosity begins to rise and this increase of viscosity becomes more and more rapid as the density is progressively increased. At 140° Tw. the viscosity is about 200,000 times that of water and the solution is a very viscous, slow-pouring, syrupy liquid—the common form of " water-glass."

Sodium silicate solutions of ratio 3·3 : 1 have a very low viscosity until a density of about 70° Tw. is reached, from which point the viscosity begins to increase very rapidly. At 80° Tw. it is about 150 times, and at 84° Tw. about 800 times, that of water. The rate of increase of viscosity as the concentration is raised above 84° Tw. is so great that the liquid passes into the form of a jelly with a change in density of only a few degrees Twaddell. It is, therefore, not practicable to prepare a stable solution of sodium silicate of ratio 3·3 : 1 having a higher density than about 84° Tw. The viscosity of the strongest solutions of this grade commercially obtainable is

thus about 800 times that of water, that is, very much lower than the viscosity of the common 2·0 : 1 ratio silicate.

Sodium silicate solutions of ratio 3·95 : 1 are the highest ratio silicates commercially available. They show an even more sudden increase in viscosity than do solutions of 3·3 : 1 ratio silicate, and they show this increase at a lower concentration. At 50° Tw. the viscosity is not greatly different from that of other salt solutions ; at 60° Tw. it has begun to increase, being about 100 times that of water, while at 63° Tw. it is about 1,000 times that of water, and the solution passes into a jelly very readily by evaporation of a very small proportion of its water content. Silicate of this ratio is therefore not supplied at concentrations greater than 60° Tw., at which concentration its viscosity is about 100 times that of water.

The viscosities described above are those of the silicate solutions at ordinary atmospheric temperatures. At higher temperatures the viscosities are greatly reduced, and at lower temperatures they are increased.

Setting Time.—The sodium silicate solutions used as adhesives depend for their setting upon evaporation into the porous surfaces which are to be united, and the actual adhesion is achieved by the passage of the silicate from the liquid to the solid state (jelly or glass). From the explanation given under the heading " viscosity " it follows that the high ratio silicates set by a smaller loss of water than the low ratio silicates. Other conditions being equal, the high ratio silicates are therefore more rapid-drying than the silicates of lower ratio. On the other hand, the high ratio silicates have little or no adhesive strength until they are dry, while the low ratio silicates, although they are slower setting, have a certain adhesive strength even while wet.

" **Tack.**"—The " tack " or stickiness of an adhesive is by no means the same as its viscosity. Tack in an adhesive holds two surfaces together, whilst the adhesive is still wet, against a force tending to pull the surfaces apart. Sodium silicate has relatively little tack and therefore the surfaces being joined should preferably be held together until dry, or at least not disturbed until dry. All forms of sodium silicate are less tacky than such adhesives as animal glue or dextrin, but the denser, more alkaline forms have sufficient tack to overcome the tendency of certain surfaces to spring apart.

Solubility.—When once sodium silicate has dried out of solution it is not easy to re-dissolve it. The higher the ratio of the dried silicate the more difficult it is to re-dissolve. No sodium silicate films, however, can be called really waterproof, though they are quite resistant over long periods to the moisture present in the atmosphere.

Alkalinity.—All the sodium silicates are decidedly alkaline, and in certain types of work this property may cause staining. The high ratio silicates contain less alkali than the low ratio silicates, and as they also dry more rapidly, there is much less likelihood of staining in their use than in the case of the more alkaline silicates. The term "neutral" is sometimes applied to high ratio silicates, but this is really a misnomer, as they all have a definitely alkaline reaction.

General Properties of Sodium Silicate as an Adhesive.—In the preceding paragraphs the differences between the various solutions of sodium silicate have been considered. Some properties possessed in common by all the solutions used as adhesives will now be considered.

(1) *General.*—All sodium silicate solutions are clear, colourless, odourless liquids. They are non-poisonous and non-inflammable.

(2) *Strength of Bond.*—When dried, all sodium silicate films are very strong. They are less strong than the best animal glues, but stronger than starch pastes; they have a tensile strength of several hundreds of pounds per square inch.

(3) *Rigidity.*—All dried sodium silicate films are very hard and brittle. They impart rigidity and strength when used for joining soft materials. This is frequently an advantage but may be a disadvantage when great flexibility is required.

(4) *Permanence.*—Sodium silicate solutions are quite stable, and in metal drums they may be kept for years without deterioration. Sodium silicate films are not absolutely permanent in air. They are slowly decomposed by the carbon dioxide of the atmosphere, and this effect restricts the use of silicate as an adhesive for wood. On the other hand, paper goods made with sodium silicate have been found to retain their strength for many years.

(5) *Heat Resistance.*—Sodium silicate films are not adversely affected by heat. The material is, indeed, a very effective fireproofing agent.

(6) *Sterility.*—Sodium silicate is purely inorganic and sterile. It cannot support the growth of animal or vegetable organisms and it is repellent to insects which feed on films of animal and vegetable glues.

Choice of Sodium Silicate as an Adhesive.—It will be seen from the preceding sections that the name "Sodium Silicate," far from

representing a single material, is applicable to a large range of solutions having widely different compositions and properties. When selecting an adhesive for any particular work, therefore, it is not sufficient to consider whether " sodium silicate " is suitable ; each of the numerous varieties of sodium silicate must be considered. By comparing the properties required in the adhesive with the properties of the various silicates as they have been outlined in the preceding paragraphs, it will frequently be found that one or other of the sodium silicate solutions is satisfactory for a particular purpose. Some of the chief adhesive uses of sodium silicate, and the considerations which govern the choice of the correct variety, are given in the following sections.

In the manufacture of *corrugated paper board* sodium silicate is almost invariably employed as the adhesive. For this purpose its low cost and quick set are of great value, while the rigidity which it imparts to the paper makes it the most suitable of all adhesives. The strength of the bond made by the sodium silicate between the corrugations and the backing paper is greater than the strength of either paper ; there is thus no advantage in using a stronger adhesive.

In this work the possibility of staining owing to the alkalinity of the silicate is not a serious objection, since most of the papers used are brown, but even so, one of the less alkaline silicates is to be preferred as being less likely to stain the paper. The machines work at high speed and the adhesive must dry in a few seconds, so that the board is stiff when it comes to the cutter. One of the rapid-drying high ratio silicates is therefore indicated. The viscosity of the adhesive must be such that it does not penetrate the backing paper, nor spread from the tips of the corrugations to which it is applied. A moderate viscosity is thus required. This excludes the highest ratio silicates of low viscosity. Sodium silicate having a ratio of about 3·4 : 1 and a density of about 79° Tw. has the correct viscosity. It also possesses the other requirements of sufficiently rapid drying rate and small tendency to stain. It will be realised, however, that the type of paper and the speed of the machine may necessitate slight modifications in the adhesive. Such modifications are achieved by small variations in the density and ratio of the sodium silicate, but these should never vary very far from the standard ratio of 3·4 : 1 and density of 79° Tw.

For joining together two, three or more plies of the same paper, or for covering a thick cheap paper with a good quality facing paper, or for *laminated paper* in general, sodium silicate is extensively used. The general requirements of the adhesive for this class of work are rapidity of drying and ease of application by rollers. When sodium silicate is used, it usually has a ratio of 3·3 : 1 or 3·4 : 1 and a density

between 75° and 85° Tw. For some types of board, however, *e.g.*, photographic mounts, the possibility of alkali finding its way to the surface is sufficient to preclude the use of silicate of soda. In certain cases quite thin laminated papers are required to show good bending properties, and here again there are objections to the use of sodium silicate. In a great many cases, however, sodium silicate will be found the most satisfactory of cheap adhesives.

Paper tubes may either be spirally wound or straight wound. In the former type of winding there is a continual force tending to pull sideways on the newly formed bond. An adhesive that is very sticky before it dries is required, and sodium silicate is not used. In straight wound tubes silicate is much used both for machine winding and hand winding. The type of sodium silicate most generally employed has a ratio of 3·4 : 1 and a density of 75° to 79° Tw. The material is quick-drying and imparts great hardness to the tubes, but the hardness is developed only after drying, which may be effected by hot air.

Sealing the bottoms and tops of *cartons* containing packeted goods is most often done by machinery, but sometimes by hand. Machines vary greatly in design, but most of them are arranged to maintain a light pressure on the sealed carton for a short time, thus enabling sodium silicate to be used. Sodium silicate of ratio 3·3 : 1 or 3·4 : 1 and density 75° to 85° Tw. will again prove to be satisfactory in many cases. It is sometimes found that frequent stoppages of the machines are necessary, and this may result in inefficient sealing of those packages which have had the flaps glued but not brought together when the machine stopped, since the silicate will dry during a stoppage of a few seconds. In order to overcome this difficulty, a slower-drying and tackier form of silicate may be used, *e.g.*, 2·9 : 1 ratio and 100° Tw., or even 2·5 : 1 ratio and 112° Tw. These grades are sufficiently slow-drying to allow for most stoppages of the machine. The adhesive on the packages leaving the machine may not be dry, but it will probably be sufficiently tacky to enable the packets to be stacked or parcelled without coming unstuck. For sealing large cardboard boxes or fibre containers, sodium silicate of 2·9 : 1 ratio and 100° Tw. density has sufficient tack to hold the flaps until they dry, in a few minutes. In some cases a thicker type, such as silicate of 2·5 : 1 ratio and 112° Tw. density is used, and in other cases a thinner type, such as silicate of 3·3 : 1 ratio and 84° Tw. density, is preferred. The actual choice is determined partly by personal preference, partly by the type of cardboard, and partly by the method of stacking the sealed boxes. As this work is often done by hand, the conditions of application are not so well defined as in machine application, and there is more latitude in the choice of adhesive.

Labelling by hand or by machinery calls for an easily applied adhesive that will dry quickly without soaking through thin labels. Silicate of soda of medium ratio (3·3 : 1 or 3·4 : 1) can be used and gives satisfactory adhesion on paper, wood or tin. The colours used in printing labels are, however, in some cases sensitive to alkali and there is a risk of discoloration if sodium silicate is used for labelling. Although an ample range of alkali-resistant colours is available, some labellers prefer to be on the safe side and do not use silicate of soda. Where labels are printed in black and white, the danger of affecting the colour does not arise and silicate may safely be used. For labelling glass bottles, *e.g.* beer bottles, sodium silicate is not used, as it sticks the labels so strongly that they cannot be removed when the bottles are washed prior to refilling.

For *wooden articles* which are required to be permanent and to have a high strength, sodium silicate is not a suitable adhesive. For such work as cabinet-making, sodium silicate would be too weak and too perishable, but it is employed successfully in certain woodworking jobs, as for instance in gluing the joints of cheap wooden boxes. It may also be used quite satisfactorily as the adhesive in the manufacture of plywood, but here again other more permanent adhesives are advisable if a long life is expected. If sodium silicate is used, the bond will weaken after one or two years. The type of sodium silicate used for wood gluing has a ratio of 3·3 : 1 and a density of 84° Tw.

Sodium silicate can be used for joining materials other than paper and wood, provided that these materials have sufficient porosity to allow that small loss of moisture which is necessary for the setting of the silicate. Thus, asbestos is treated in the same way as paper to form asbestos boards or corrugated asbestos. The type of silicate used has a ratio of 3·3 : 1 and a density of 84° Tw. Cloth fabrics can be stuck to paper, or paper to metal, or metal to asbestos, and most other combinations in which one of the materials is sufficiently porous may also be effected by means of silicate of soda.

Adhesive Mixtures containing Sodium Silicate.—Sodium silicate adhesives can be modified by admixture in two ways: (*a*) by the addition of materials not in themselves adhesives, but which alter the properties of the silicate, or (*b*) by admixture with other adhesives. Sodium silicate is also employed as a source of silica gel in certain mixed adhesives; in these, the sodium silicate is destroyed by means of an acid and no longer has its intrinsic adhesive properties. Such adhesives are described on pages 68 to 71.

The addition of clay to sodium silicate is one of the commonest methods of modifying its properties. A finely powdered dry (but not burned) clay added to a sodium silicate solution increases the

viscosity and the setting rate of the silicate. By adding different amounts of clay and water to a sodium silicate solution it is possible to alter the viscosity and the setting rate independently, so that slower-setting or faster-setting adhesives of lower or higher viscosity than the original silicate can be prepared. Finely powdered calcium carbonate in the form of whiting or ground limestone is also used as an addition to silicate solutions, but it does not remain in suspension as well as the clay.

Silicate solutions may be mixed with other adhesive solutions to give a mixed adhesive having properties intermediate between those of the two separate adhesives. Starch may be incorporated with silicate solutions, either by mixing the already prepared starch solutions with a silicate solution, or by heating a suspension of starch in water with sodium silicate until the solution clears. Widely different proportions of starch and silicate may be employed. A particular case of a starch-silicate adhesive is described on page 156.

Dextrin-silicate mixtures are sometimes of value, as they are tackier than, and not so brittle as, silicate alone, and are stronger and more rigid than dextrin alone. Dextrin solutions may be mixed in any proportions with silicate solutions to give mixed adhesives having the properties of each constituent roughly in the proportion in which it is present.

Sodium silicate is also a valuable addition to casein adhesives. Very water-resistant casein glues are made with lime, but these suffer from the disadvantage that the glue remains workable for only a very short time. When the amount of lime taken is that which gives the maximum water resistance (about 30 parts of hydrated lime to 100 parts of casein) the working life is less than an hour. By the addition of alkaline salts, however, the working life is extended. Sodium silicate is the best alkaline salt to use, because it gives the greatest effect on the working life. The addition of 50-100 parts of silicate of soda (3·3 : 1 ratio and 84° Tw.) is sufficient to extend the working life to about one day. The addition of greater amounts of sodium silicate will give a still longer working life. Unlike the other alkalis that may be added, sodium silicate is itself an excellent adhesive and therefore may be mixed in any proportions with the casein-lime adhesive to give a mixture having intermediate properties. An increase in the silicate content of the adhesive will give it a longer working life and reduce its cost, but will impair its water-resistance.

Sodium silicate may also be mixed with rubber latex, which makes the film more flexible than with silicate alone.

The use of sodium silicate in conjunction with rosin is described on page 142.

The foregoing description of the properties of sodium silicate and the uses of the various types for different adhesive purposes may help users of adhesives to decide whether sodium silicate will be of service to them, and if so, what type of silicate will be most suitable for their purpose. The range of silicates commercially available is sufficient to enable the correct type to be purchased ready for use, but in special cases, one or other of the various ways of changing the properties may be used.

To summarise, the principal advantages of silicate of soda as an adhesive are its high strength, low cost and quick set. Its principal disadvantage is its alkalinity. Its property of forming a hard rigid film and its relatively low tack are sometimes advantages, and sometimes disadvantages.

CHAPTER XIII.

ECONOMIC ADHESIVES FOR GREASY, VARNISHED AND METALLIC SURFACES.

For effecting the adhesion of materials which are resistant in varying degree to water-containing solutions, the cellulose type of adhesive in which the solvent is a non-aqueous one may, of course, be employed, but it is obvious that if a water-soluble material can be used with technically satisfactory results, numerous advantages will be gained, these advantages including cheapness, facility of application and reduced fire risks.

On frequent occasions in earlier pages of this book indications have been given as to how the lack of affinity of aqueous adhesive solutions for the more resistant surfaces can be overcome. These methods may be summarised as follows :—

(1) With aqueous adhesives : (*a*) By the addition of wetting agents (soaps, sulphoricinoleates, sulphonated products, etc.) which reduce the surface tension of the liquid and consequently facilitate its impregnation of the surface to which it is applied. (*b*) By the use of a material containing free acid or free alkali (obtained by incomplete neutralisation of the solution or by the addition of extra amounts of acid or alkali). What happens in this case is that the surface of the material to which the adhesive solution is applied is attacked by the acid or alkali, the resultant roughened surface affording adequate anchorage for the adhesive solution. The degree of this " etching " by the acid or alkali is in most cases far too slight to have any undesired effect on the strength of the coated material and, wherever possible, this is the most convenient system to use when applying water-soluble adhesives to resistant surfaces. For instance, a high-strength synthetic alkaline starch adhesive paste of type C-2 can be used for cementing practically anything. (*c*) By the addition of materials capable of imparting to the aqueous adhesive a certain plasticity or a certain hygroscopic character. Glycerin, glucose and emulsifying oils are some examples of this type of material. Chlorides are also useful, but have certain disadvantages, as has been pointed out earlier. (2) In the case of adhesives which are solutions in organic

solvents, their working properties can be enhanced by the addition of oils or heavy solvents possessing plasticising properties.

A very frequent industrial problem is the application of paper or similar material to untreated metallic surfaces, and this problem in adhesion can be considered in two divisions. First, where the metal is not fragile, has a non-greasy surface and has a greater or less affinity for water; and secondly where the metal is fragile and water glues result in unsatisfactory adhesion. In regard to the first case, before discussing the question of special formulæ, it should be pointed out that the great majority of the problems can be solved by the adoption of the ordinary starch adhesives discussed in Chapter VIII of this book.

All the *starch adhesives* described in Formulæ A-1 to A-15, with the exception of those made by the aid of calcium chloride, are perfectly suitable. Those dealt with later in Chapter VIII, and which contain a high percentage of soap, are not quite so suitable, as they adhere less satisfactorily to metals.

To avoid risks of staining, oxidation, etc., the starch adhesives obtained by oxidation treatment are particularly to be recommended, in conjunction with the sodium fluoride-formaldehyde mixture given on page 77, these being suitable for the sticking of paper to galvanised sheet, ordinary sheet iron, etc. If the adhesion obtained with these pastes is inadequate owing either to the greasy nature of the metal or the fact that the paper is slightly varnished or slightly parchmentised, then the pastes discussed on pages 64 to 70 should be used. These, by their greater or lesser content of free caustic soda, of salts formed in the production process, or of silicate of soda, assure better adhesion by their slight pickling action and attack on the surface of the material (Formulæ A-2, A-5 and A-6 for example).

The *dextrin adhesives* can be used for similar purposes as the products just discussed, and in particular for the treatment of biscuit boxes and other galvanised metal articles. The adhesives given under Formulæ B-1, B-2, B-3 and B-4 are remarkably well suited, owing to their good rate of drying and their property of forming what may be described as a corrosion-resistant varnish. With other high-concentration dextrin adhesives, *e.g.*, those of types B-7, B-8, B-9 and B-10, the efficiency for work on metal can be increased by the addition of a small quantity of glycerin or glucose on account of their plasticising character.

All the *synthetic strong starch and casein adhesives* adhere very well to metals which are not too greasy and give results superior to those obtained with the ordinary starch products or dextrins.

From the information given in regard to each type of adhesive

on preceding pages and the summary above, the manufacturer should be able to select the product most suitable for his purpose from the viewpoint of efficiency and price. A further important factor in deciding upon the choice of an actual adhesive is, of course, the advisability of selecting one type of paste which can be used for a variety of applications.

As an instance of a more difficult problem in the adhesion of paper to metals, the manufacture of metallised paper by the attachment of a sheet of laminated aluminium to a paper backing may be mentioned. This type of product has become very important in recent years owing to the novel decorative effects obtainable and its strength and waterproofness. Aluminium, however, is not only resistant to many kinds of chemical attack, but it is one of the most difficult materials to wet with aqueous solutions. The adhesive used should naturally possess good affinity for the aluminium, without any oxidising effect, whilst it is highly important that it should contain no chlorine products. The manufacture of this type of aluminium paper is carried out, briefly, as follows:—The paper unrolling from its feed spool passes through the vat containing the adhesive solution. The aluminium foil meets the paper just as it leaves the bath and the two layers in juxtaposition pass under a high-pressure calender to assure good adhesion, a smooth surface and to squeeze out air bubbles and any excess of paste. The metallised paper then passes into a horizontal stove and after drying is wound on to a spool. It should be noted that perfect drying of the adhesive is essential for, if the metallised paper on leaving the stove contains any imprisoned residual moisture, the wrapped product acts as an electrolytic cell, the electrolytic changes causing oxidation of the aluminium and consequently loss of the metal's lustre.

For this type of work a starch adhesive is both the simplest and the most economical. Of the various types of starch adhesive discussed in Chapter VIII those of Formulæ A-1 to A-4 are suitable. It may be found, however, that these pastes possess insufficient adhesion for the laminated aluminium, and in this case an accessory adhesive is essential. *Sodium silicate* is the one recommended. When used by itself, sodium silicate is impracticable for working on aluminium since the dry film is too friable and the adhesive is too basic, but when employed in small quantities only as a constituent of a modified starch adhesive, the final product has all the advantages and none of the disadvantages of the two adhesives individually.

The type of adhesive which is specifically recommended by the writer for metallised paper is the concentrated cassava starch paste of type A-13, final additions of chloride or sodium fluoride and

formaldehyde being omitted. The paste is allowed to cool in the mixer before the sodium silicate is added. This procedure avoids coagulation of the silicate and also precipitation of the starch by the silicate. When the paste has cooled, the dry crust which has formed on the top is removed, the paste then mixed a little to give it a certain fluidity, then water added to increase this fluidity, and finally the 35° Bé. sodium silicate in the proportion of 22 kilogrammes per 100 kilogrammes of undiluted initial adhesive paste.

Since sodium silicate has a certain antiseptic efficiency, the usual quantities of formaldehyde can be somewhat reduced. If the paste is to be used very soon after making, the formaldehyde solution can be omitted altogether (Roger Dulac Processes).

Formula E-1.

Cheap Adhesive for Aluminium and other Metals.

Water,	750	Heat to 85° C. and allow to cool.
Caustic soda lye, 36° Bé.,	0·450	
Hydrogen peroxide, 12-vol.,	3·500	
Cassava starch,	250	
Water,	300	Mix.
Sodium silicate, 35° Bé.,	220	Mix.
Formaldehyde solution, 30 per cent.,	2.500	Mix.
Water,	3	

Owing to the presence of free silicate, which tends to precipitate starch, this adhesive solution should be protected from too low temperatures during storage. It should not be made, if possible, earlier than two months before being used. With certain qualities of aluminium, the percentage of silicate in this formula can be reduced.

Water-basis adhesives without organic solvents, particularly *ordinary glue*, can also be applied satisfactorily for pasting paper, etc., on varnished, lacquered, etc., surfaces, by the addition of *plasticising oils*, the final products being aqueous emulsions. Castor oil, the cheapest of these plasticising products, is perfectly satisfactory technically. Use is made of a sulphoricinoleate as emulsifying agent, whilst the emulsion, especially when containing high percentages of oil, can be protected by the further addition of colloidal clay. The film obtained on drying-out is very plastic, and is similar in some respects to the films obtained from non-aqueous solutions (Roger Dulac Processes).

The sulphoricinoleate prevents the glue from setting and gives a liquid cold glue. It is preferable, for this type of adhesive, to use cheap, poorly gelatinising glues, block glue for instance. Since 90 per cent. acid ammonium sulphoricinoleate contains free castor oil, the incorporation of additional quantities of the latter may be unnecessary, as in Formula E-2.

Formula E-2.

Cheap Adhesive for Greasy, Varnished or Lacquered Surfaces.

Ordinary glue, . . .	100	Dissolve on the water-bath.
Phenol, ...	2	
Water, ...	200	
90 per cent. acid amm. sulphoricinoleate, . . .	60	

The quantity of water given in this formula is only approximate and can be varied in accordance with the actual gelatinising power of the glue used. The carbolic acid (phenol) functions purely as an antiseptic. This formula, which is the simplest of its type, yields an adhesive suitable for practically all the cases now under consideration and even when working with very thin paper there is no risk of fatty matter staining through. The paste can be diluted with cold water as needed.

If, for certain applications, the degree of adhesion obtained by this emulsion is thought inadequate, the quantity of castor oil can be increased somewhat. The extra oil is added and the solution heated again on the water-bath until complete dispersion has been obtained.

For materials which are very greasy and very resistant to adhesives, paraffined paper for example, Formula E-2 can be improved by the addition of *solvents* belonging to the class of aromatic hydrocarbons, that is, benzene, toluene or better still, xylene, these being added to the lukewarm adhesive and well stirred in. Although immiscible with water, these hydrocarbons are also dispersed by the sulphoricinoleate. There is a limit to the quantity of hydrocarbons that can be used, because above a certain point the adhesive assumes a mayonnaise-like consistence and is not easily worked.

Xylene is used in preference to benzene and toluene because it is a better solvent for paraffin. It will be noted from Formula E-3 below that the quantity of sulphoricinoleate is considerably less than that in Formula E-2. This is because, in use, this adhesive is imprisoned between two rather impermeable surfaces, and this naturally slows up the rate of drying. It is consequently advisable

to aim at a film which is less plastic and drier than that formed by the product made up by Formula E-2. Care should be taken in any dilution that may be carried out on the product obtained by Formula E-3. If this dilution is carried too far there is always the danger of the emulsion breaking and the solvent separating out.

Formula E-3.

Cheap Adhesive for Paraffined Papers.

Ordinary glue, . . .	100	Dissolve on the water-bath.
Water, ...	150	
90 per cent. acid amm. sulphoricinoleate, . . .	10	
Xylene, ...	100	Add to the tepid solution and agitate vigorously.

An adhesive made according to Formula E-3 is serviceable for working on practically every type of greasy, varnished or lacquered surface, but there is one special case in which the use of a hot glue is advisable. This is in assembling articles such as novelties, toys, jewellery, etc., in which it is better that the adhesive should be perfectly colourless and capable of setting instantaneously. In such a case the following formula is recommended. The gelatin used should be of the edible quality.

Formula E-4.

Hot Glue for Greasy, Varnished and Lacquered Surfaces.

Water, ...	800	Dissolve on the water-bath.
Transparent gelatin, . .	200	
Phenol, ...	2	
90 per cent. acid amm. sulphoricinoleate, . . .	20	

The actual quantity of the wetting agent (the sulphoricinoleate) in the mixture can be varied to suit the exact nature of the article to be treated. If the addition of a solvent to this mixture be thought advisable, use should preferentially be made of carbon tetrachloride, which is non-inflammable.

A number of rather difficult technical adhesion problems can be solved by the employment of *rosin admixed with a plasticising oil*, castor oil for preference. Treatment of varnished box cardboard on a high-speed machine is an instance of the type of application for

which these glues, which are easy to make, cheap, and which set practically instantaneously, are very serviceable. The oil is placed at the bottom of any convenient receptacle and the rosin, coarsely broken into lumps, is added. Solution is effected by heating over a direct fire, with occasional stirring of the mass (Roger Dulac Processes).

With a rosin of clear W-G quality and a first-pressing castor oil, about 55 kilogrammes of the oil should be used for each 100 kilogrammes of the rosin, to obtain after cooling a fine, pale, transparent glue which draws out in long threads and which possesses an extraordinarily sticky character. Made in this form the glue is best applied by means of a spatula and is suitable for such purposes as making the joint in the change-over from one spool of paper to another on rotary printing machines, the manufacture of fly paper, etc.

If a second-pressing castor oil is used, the glue is not so transparent. Attempts at replacing the castor oil by linseed oil or glycerin will result in decidedly inferior products. Blown castor oil or blown rape oil give better results than untreated castor oil, but the advantage obtained is hardly adequate to outweigh the added cost of the materials.

It will be appreciated that the material just described does not dry-out, but remains permanently sticky. By reducing the proportion of castor oil, however, a material which has to be melted before use but which sets hard after application is obtained. Such a product is valuable for the sticking of waterproof transparent cellulose wrapping paper and of metals and varnished papers.

The following are the basic formulæ for the two types of glues just discussed :—

FORMULA E-5.

PLASTICISED ROSIN GLUE FOR USE IN THE COLD.

Castor oil, ...	55	Melt together over a small free flame.
Rosin, ...	100	

FORMULA E-6.

INSTANT-SETTING PLASTICISED ROSIN GLUE FOR HOT USE.

Castor oil, ...	17	Melt together over a small free flame.
Rosin, ...	100	

If it is more convenient that this type of product be of such a consistence that it can be applied by a brush instead of by a spatula, Formula E-5 can be modified by thinning with methylated spirits. After application, the alcohol evaporates, the final film being identical with that left by the original formula. If it is desired not only to

produce an adhesive capable of application by the brush, but one which will leave a hard dry film, then Formula E-6 is the one to be modified by the additional use of methylated spirits (see Formula E-7).

Formula E-7.

Plasticised Rosin Glue in Fluid Form.

Castor oil,	17	Melt together over a small free flame.
Rosin,	100	
Industrial methylated spirits,	50	Bring to the boil and add to the hot mixture of rosin and oil.

The temperature of the oil-rosin mixture to which the boiling spirit is added should be from 75° to 80° C. If its temperature be higher, too much alcohol will be lost; if lower, the rosin-oil mass will set into a solid block dissolving in the alcohol only with the greatest difficulty. In view of the highly inflammable nature of alcohol vapours, the utmost precautions should be taken to ensure the absence of a naked light or the possibility of spark formation in this process.

Very sticky compositions for use on fly papers, plasters, etc., can also be manufactured from *mixtures of rosin and rubber*. Benzene is a solvent both for rosin and for rubber, and in the recommended process of manufacture from 5 to 8 per cent. of crêpe rubber, depending upon the viscosity and plasticity desired in the finished mass, is added to a saturated solution of rosin in benzene, the stickiness of the product being enhanced by the final addition of a little castor oil.

Formula E-8.

Sticky Rubber-Rosin Glue.

Benzene,	60	Dissolve.
Rosin,	100	
Castor oil,	3	
Crêpe rubber,	5	

If this material is to be made in paste form, calcium carbonate should be added to the benzene before the introduction of the crêpe rubber.

If the castor oil and the rosin are added separately to the benzene, the film obtained on application of the adhesive is soft even when only 3 per cent. of castor oil is used. If, however, the rosin and the oil are first melted together, before addition to the benzene, the film obtained is hard.

A particularly interesting and novel adhesive composition can be

made in the form of an *aqueous emulsion of plasticised rosin* by taking advantage of the emulsifying powers of *colloidal clay,* which have been referred to earlier in this work (Roger Dulac Processes). The composition obtained is opaque, creamy, ropy, very sticky and cheap. It is particularly serviceable for use on soft flexible materials such as linoleum, rubber flooring and cloth linings in coach work. Since it possesses a high degree of " body," it fills up perfectly any inequalities in the surfaces of the materials being joined. It is of especial interest for automobile coachwork since, owing to its viscosity, it does not penetrate and discolour soft furnishings.

The hardness of the film produced by a composition of this type can be increased by reducing its content of castor oil, but the film always remains flexible. The effect of bentonite (colloidal clay) in this type of product is remarkable. Whilst the film produced by a mixture of 5 parts by weight of castor oil and 100 parts by weight of rosin is hard and has tendency to crumble, the film left by a similar mixture prepared in the form of an aqueous emulsion with the help of bentonite remains perfectly plastic owing to the property possessed by the bentonite of retaining firmly some of the water and the alcohol used in the emulsion. For reasons of economy, and also to increase the body of the composition, dilution is effected with a mixture of water and alcohol and not with alcohol alone.

With refined bentonites possessing high swelling power, direct mixture with water is difficult. The clay absorbs the water with such avidity that small lumps are immediately formed, these lumps remaining resistant to disintegration even on prolonged boiling. For this reason the bentonite is first wetted with alcohol and the water added only after a homogeneous mixture of the clay and alcohol has been obtained. The bentonite readily mixes with the rosin-oil mass provided it is added after mixture with the alcohol and water. If all, or the bulk of, the water be added to the batch last, satisfactory emulsification is obtained only with exceeding difficulty. The proportion of bentonite to water will vary from 1 : 10 to 1 : 15, according to the quality of the bentonite used.

The properties of this adhesive emulsion can be modified by varying the proportions of the various ingredients utilised. Increase in the quantity of castor oil is accompanied by an increase in the plasticity and stickiness of the emulsion. The alcohol diminishes the viscosity of the composition but facilitates the emulsification process, since it is a solvent both for the castor oil-rosin mixture and for the water. The smaller the amount of oil the greater is the quantity of alcohol that should be used if a glue is to be obtained which is not too thick and which spreads well. Increase in the quantity of water-bentonite

increases the viscosity and thickness of the composition. A representative formula for this type of adhesive composition is given below :—

FORMULA E-9.

EMULSIFIED ROSIN ADHESIVE FOR COACHWORK, LINOLEUM, RUBBER FLOORING, ETC.

Castor oil,	5	Melt over a small free flame and allow to cool to 75°-80° C.
Rosin,	100	
Refined bentonite,	10	
Refined bentonite,	2·5	Boil, add to the above mixture at 75°-80° C. and emulsify.
Methylated spirits (Industrial),	75	
Water,	25	

The purpose of adding a quantity of the bentonite to the initial mixture of castor oil and rosin is not only to reduce the cost of the composition but also to increase its hardness and to facilitate the introduction and dispersion of the remainder of the bentonite. If a somewhat more plastic adhesive is required, the quantity of bentonite is reduced.

It will be appreciated that the mechanical factor is of great importance in making this type of product. The mixer used should be fitted with a really efficient agitator and the agitation should be continued until the batch has completely cooled down.

CHAPTER XIV.

CELLULOSE ADHESIVES.

THE normal constituents of a cellulose solution used for adhesive purposes are a cellulose ester, a resin, a solvent of medium boiling point, a diluent, a solvent of high boiling point and a plasticiser. This type of adhesive is used for working on material very resistant to aqueous adhesives, and where joints that are very strong and waterproof, and at the same time flexible, are required.

Of the two types of cellulose ester generally available in industry to-day it is the nitrate which presents the greatest degree of interest to the maker and user of adhesives and in regard to which most experience has been accumulated. Cellulose acetate solutions undoubtedly have value as adhesives for special purposes, but their price is usually higher than that of cellulose nitrate solutions.

For reasons of economy use is most often made in the adhesives industry of nitrocellulose film scrap that has been freed from its coating of photographic emulsion. This scrap has the added advantage of containing, in addition to the cellulose nitrate, the bulk of the camphor that has been incorporated as a plasticiser in making the film. Collodion-quality cellulose nitrate offers the advantage of enabling the production of adhesive solutions containing a higher percentage of solids than those with film scrap. The principles involved in the preparation of these solutions are the same, however, whether collodion cellulose nitrate or film scrap is employed.

The addition of *resins* to these cellulose solutions is made for various reasons. In the first place they are cheap and so enable reduction in the production costs of these adhesives. Secondly, the presence of resins influences the viscosity of cellulose nitrate solutions to but a very slight degree ; consequently their incorporation enables the production of solutions of improved body and density, which leave thicker films than do solutions containing no resins. Finally, the presence of resins improves the hardness, lustre and sticking power of cellulose nitrate films.

Although quite a variety of natural and synthetic resins finds

application in cellulose nitrate solutions for use as lacquers and varnishes, the adhesives maker can satisfy all his requirements by selection from the following three, which are given in order of increasing price and quality, namely: ordinary rosin, coumarone resin and ester gum.

Rosin itself is of course the cheapest, but it suffers from the drawback that it is composed largely of free abietic and pimaric acids, which can occasionally be a source of trouble in adhesive solutions. Further, ordinary rosin is deficient in hardness.

Coumarone resin is better, being harder, more resistant to chemical and physical attack and superior in general solubility properties. It is, of course, rather dearer than ordinary rosin.

The best resin of all for adhesives making is ester gum, the product of the reaction between glycerin and rosin. It can be used in proportions up to three-fourths of the weight of the cellulose nitrate. It is not advisable to increase the quantity of ester gum beyond this point or the film will be on the soft side. If additional resin is to be used, it is better to add a little of the harder type. For general purposes a mixture of ester gum and coumarone resin in the ratio of two to one by weight is probably the best of all.

A complete account of the solvents and plasticisers used in making cellulose nitrate solutions is out of the question here and room can be found only for those essential points which have a bearing on the making and use of cellulose nitrate solutions as adhesives, keeping in mind also the necessity for these solutions being as simple and as cheap as possible. (For greater detail the reader is referred to "Solvents" (Third Edition), by T. H. Durrans, D.Sc., F.I.C. (Chapman and Hall, Ltd., 10/6 net)).

The liquid constituents of cellulose solutions can be classified broadly as true solvents, diluents and plasticisers. The *true solvents* are liquids capable of dissolving cellulose nitrate. The *diluents* are not, in general, solvents for cellulose nitrate when employed alone, although they may act as solvents in the presence of other materials—they are added mainly because they are cheaper than the true solvents and allow of the production of lower-priced adhesives. The *plasticisers* are high-boiling, practically non-volatile substances which do not evaporate, as do the true solvents and diluents, but remain in the dried film upon which they confer the properties of elasticity, flexibility and greater adhesiveness. To a certain extent the hardness of the dried film decreases as its content in plasticiser increases but, as shown above, this drawback is countered by the addition of resins. In any event, a cellulose film which is too hard and dry when spread over very even surfaces tends to form a glaze which can be peeled off

fairly readily. The presence of the plasticiser, further, usually improves the gloss and the watertightness of a cellulose film, whilst a number of the plasticisers are definitely fire-retarding materials. With the exception of camphor, which is a solid, most of the plasticisers used in making cellulose adhesives are liquids.

The numerous materials available can be classified into the following groups according to their chemical composition :—

(1) Aromatic hydrocarbons: Benzene, toluene, xylene, solvent naphtha, etc.
(2) Aliphatic hydrocarbons: Petrol, petroleum ether, white spirit, etc.
(3) Chlorinated hydrocarbons, etc.: Ethylene chlorhydrin, chloroform, carbon tetrachloride, trichlorethylene, etc.
(4) Alcohols: Methyl alcohol (methanol), ethyl alcohol, butyl alcohol (butanol), amyl alcohol, benzyl alcohol, etc.
(5) Ketones: Acetone, methyl ethyl ketone, etc.
(6) Esters: Methyl, ethyl, butyl, benzyl, etc., esters of acetic, formic, lactic acids, etc.
(7) Glycols: Ethylene glycol, acetylated ethylene glycols, methyl, ethyl and butyl ethers of ethylene glycol, etc.
(8) Hydrogenated products: Cyclohexanol, methyl cyclohexanol, their acetates, etc.
(9) Furfural derivatives: Furfural, furfuryl acetate and alcohol, etc.
(10) Plasticisers: Triacetin, triphenyl phosphate, tricresyl phosphate, ethyl phthalate, butyl phthalate, camphor, etc.

After actual solvent power, the most important property of the *solvents* is their speed of evaporation. They can consequently be classified also according to their boiling-points or vapour pressures, which are corollaries of their speeds of evaporation. For instance acetone, which boils at ordinary pressures at 55°-56° C., possesses a low boiling-point and a high vapour pressure and can be considered a rapidly-evaporating solvent. It should be noted, though, that in these solvents speed of evaporation is not a property which always runs parallel with the boiling-point, and that of any two solvents it is not always the one with the lower boiling-point which has the quicker rate of evaporation.

Since a cellulose solution of the usual type contains both cellulose nitrate and a resin, it is essential that the drying solution shall contain, up to the very end of the evaporation, the solvents required to keep both these materials in solution. Otherwise, either the cellulose

nitrate or the resin will be precipitated out before the film is quite dry with not only impairment of the strength of the film but with the production of a turbidity which is referred to in the cellulose lacquer industry as " blushing."

A similar phenomenon, but from another cause, can also take place in the drying process. In evaporating, it is a well-known law of physics that a solvent withdraws heat from the surrounding atmosphere, and, if this withdrawal be at too great a rate the temperature of the surrounding air will be reduced below the dew point and moisture will be precipitated on the cellulose film. This " water blush " or " chilling " is most liable to occur when the solution contains rapidly-evaporating solvents such as ether, acetone or benzene.

When the cellulose solution is used for adhesive purposes these blushing phenomena occur, it is true, much less readily than when the solution is allowed to dry as a lacquer in the open air, but they do occur none the less even in adhesives solutions, and regard must be paid to this point in formulating such solutions.

There is another general property possessed by solvents to which attention should be drawn. Very often, a mixture of two solvents does not behave quite like a simple mixture, particularly as regards the boiling-point. In cases where something of the nature of inter-molecular attraction exists between two solvents the boiling-point of the mixture may be higher than or, more usually, lower than that of either of its two constituents alone. Such mixtures are termed *azeotropic mixtures*; if there are two constituents they are binary azeotropic mixtures; if three, as is sometimes the case, they are ternary azeotropic mixtures. An example is provided by acetone, the boiling-point of which is 55-56° C. When mixed with carbon bisulphide in the proportions of 34 parts to 66 parts by weight, an azeotropic mixture with a boiling-point of 40° C. is formed. Conversely, a mixture of 20 parts by weight of acetone and 80 parts of chloroform boils at 65° C. and thus enters the range of the medium-boiling solvents.

If by the formation of an azeotropic mixture the boiling-point is lowered, and consequently the vapour pressure and the speed of evaporation raised, the tendency of the drying film to blush will be intensified. Further, the solvent will tend to evaporate more speedily than the diluent, and this will give rise to " blushing " from the precipitation of the nitrocotton or the resin.

The employment in cellulose solutions of those solvents which are water-miscible is often discountenanced on the grounds that when present they aggravate the troubles caused by blushing, since any

atmospheric water deposited is precipitated in the body of the drying film, whilst if water-immiscible solvents only are used the water is deposited only on the surface of the film. This attitude cannot always be justified. On price grounds it is rarely possible to do without water-miscible solvents, whilst in certain cases the solvent or diluent forms with water a binary mixture of constant boiling-point. The alcohols, which are all water-soluble, and butyl alcohol in particular, are the materials most frequently employed to prevent blush by forming such binary azeotropic mixtures with water.

The presence of water in a solvent is not of necessity harmful. In certain cases, indeed, the presence of a small quantity of water improves solvent power and often explains the higher solvent powers which are possessed by certain industrial materials as compared with the same materials in the anhydrous state.

The viscosity of cellulose nitrate solutions bears a direct relationship to the solvent powers of the liquids used. Up to a certain point the addition of diluent increases the viscosity of the solution; beyond this point gelatinisation tendencies manifest themselves and, with still further addition of diluent, the cellulose nitrate is precipitated in the form of a gel.

The esters, ethyl acetate and butyl acetate in particular, are the most widely used solvents for cellulose nitrate, the first-mentioned being the cheaper material. Solvents of low boiling-point (ether, acetone, etc.) have usually the highest solvent powers and give solutions of lowest viscosity, but their rates of evaporation, and the dangers of fire, are usually too high for adhesives work.

From the particular viewpoint of the adhesives industry probably the most serviceable agent for cellulose nitrate is the azeotropic mixture of benzene or of toluene with industrial alcohol. In the former case the mixture is 68 per cent. by weight of benzene and 32 per cent. of 95 per cent. denatured industrial alcohol; and in the latter 32 per cent. by weight of toluene and 68 per cent. by weight of 95 per cent. industrial alcohol. The first-mentioned azeotropic mixture boils at 68° C. and the second at 77° C.

Although when used alone benzene, toluene and alcohol are not solvents for cellulose nitrate, yet when employed as the above mixture they swell the cellulose ester to such an extent that it requires only a small quantity of a true solvent to bring it into solution.

Most of the liquid ingredients normally present in these cellulose solutions are inflammable, the risk increasing with fall in boiling-point. Consequently, the greatest precautions should be taken to prevent accidental ignition by flames or sparks. (In the United Kingdom the preparation and storage of these cellulose solutions is

subject to Home Office Regulations (Cellulose Regulations, 1934, S.R. & O., 1934, No. 990)).

At the same time the risk in producing solutions for adhesive purposes is not usually so great as in making solutions for use as lacquers or varnishes since, in the former case the quantities handled at a time are usually comparatively small. On the same grounds toxicity risks do not loom so largely in the mind of the adhesives maker as the lacquer maker, although these risks should never be overlooked.

The *plasticising materials* can be grouped into two main divisions. The gelatinisers or plasticisers which dissolve cellulose nitrate, and the non-gelatinisers or plasticisers which have no solvent action on the cellulose ester. To be most efficient, a plasticiser should fall into the former group and it is an added point in its favour if it is also a solvent for the resin employed. In any case, of course, the plasticiser should be soluble in the various liquids used in making up the cellulose solution.

Certain plasticisers are miscible with cellulose nitrate in all proportions; others are tolerated only up to a certain limit, beyond which crystallisation phenomena are produced in the drying film if the plasticiser is a solid or an oily exudation is met with if the plasticiser is a liquid. In general, preference is given to the liquid plasticisers, though solids such as triphenyl phosphate can be used provided their proportions in the solutions are well controlled.

To the first group, the gelatinising plasticisers, belong camphor and the majority of the synthetic plasticisers, namely the esters of phosphoric and phthalic acids.

To the second group, the non-gelatinising plasticisers, belong the vegetable oils (castor oil or rape oil in particular) and the esters of linoleic and stearic acids. The interest possessed by the members of this latter group lies mainly in their low price, castor oil being the product most used. Employed in too great quantities they tend to exude from the dried film.

It is frequently possible to combine the use of members of the two groups very advantageously, in the proportion of one part by weight of gelatinisers to three or four parts by weight of non-gelatinisers.

The quantity of plasticiser used is generally from 10 to 50 per cent. of the weight of the dry cellulose nitrate, but this proportion may be increased if the amount of resin present is on the high side.

It will be recognised from what has been said above that the formulation of cellulose nitrate solutions is not a very simple matter. As a general rule, the constituents should fall into the following groups:

(1) *Light solvents* or those evaporating rapidly. These are relatively cheap, give concentrated solutions of low viscosity and assure the rapid formation of the initial film of cellulose nitrate.

(2) *Medium solvents* or those evaporating at intermediate rates. These slow down the rate of evaporation and so minimise the tendency to " water blush." They also smoothly close the gap between the light solvents and the heavy solvents. This latter point is very important in cellulose lacquers and varnishes, where smoothness in the rate of evaporation is always aimed at. In the case of cellulose solutions for adhesive purposes the importance of the intermediate solvents is not so great and their employment can be omitted.

(3) *Heavy solvents*, or those which evaporate slowly. These do not dissipate until the very end of the film deposition and so ensure perfect spreading and smooth appearance of the film. These heavy solvents in particular should be very efficient solvents both for the cellulose nitrate and the resins, whilst they should form azeotropic mixtures with water to avoid the occurrence of " water blush."

(4) *Plasticisers.*—These confer plasticity, flexibility and adhesiveness on the cellulose film. The plasticisers of the gelatinising type should preferably be solvents both for the cellulose nitrate and for the resins. The non-gelatinising plasticisers are used almost entirely for cheapness.

(5) *Diluents.*—These are added to reduce the costs of solvent mixtures. Diluents capable of exerting a slight solvent action are chosen. The speed of evaporation of these diluents should be such that they are eliminated with the heavy solvents. In any case, they should possess solvent power for the resins used in the mixture.

In the representative formulæ for cellulose solutions for adhesive purposes now to be given, film scrap has been selected as providing the most suitable form of cellulose nitrate. For the very cheap product, first given, ordinary rosin in proportion of one-third of the weight of the film scrap is used. It is much better, however, to use ester gum or, better still, a mixture of one-third coumarone resin and two-thirds ester gum. Still better, though more costly, is to use a synthetic resin of the vinyl type (for instance " Mowilith NN " made by the I. G. Farbenindustrie A.-G., or the allied products made in Canada). The alcohol and benzene, among the cheapest of the diluents, are employed in the form of the azeotropic mixture that has already been referred to. Acetone and ethyl acetate are selected as the best and most economic actual solvents for the cellulose nitrate. Ethyl acetate is given the preference on account of its higher boiling-point. The ester is added in the proportion of 25 kilogrammes per 100 kilogrammes of the alcohol-benzene mixture.

Among the slowly-evaporating solvents, ethyl lactate, butyl alcohol and butyl acetate come up for consideration. The last-mentioned is selected because it is the cheapest, is readily obtainable and has a pleasant odour. Butyl acetate, moreover, is one of the best general solvents for cellulose nitrate in any of its forms, for resins and for oils. Further, when employed in conjunction with a little butyl alcohol, it greatly reduces the possibilities of blush troubles. It is advisable always to have present a little butyl alcohol, since this material increases the solvent power of the esters, diminishes the viscosity of the solutions and prevents drying troubles, especially when large quantities of diluents are present. A good mixture to use is 15 per cent. of butyl alcohol to 85 per cent. of butyl acetate. An alternative is the azeotropic mixture 47 per cent. of butyl alcohol and 53 per cent. of butyl acetate, which boils at 117° C.

As plasticiser, castor oil alone is recommended, since the film scrap used will contain a sufficiently high amount of the gelatiniser camphor, which was used in making the original celluloid.

Formula F-1.

Cheap Adhesive Cellulose Solution.

Benzene, solvent grade,	580	Soak for 12 hours.
Denatured alcohol, 95 per cent.,	265	
Castor oil,	12	
Rosin,	30	
Film scrap,	100	
Ethyl acetate,	210	Add and mix until dissolved.

Formula F-2.

Improved Adhesive Cellulose Solution.

Benzene, solvent grade,	550	Soak for 12 hours.
Denatured alcohol, 95 per cent.,	250	
Butyl alcohol,	8	
Butyl acetate,	42	
Castor oil,	12	
Ester gum,	20	
Coumarone resin,	10	
Film scrap,	100	
Ethyl acetate,	200	Add and mix until dissolved.

If the film scrap has been swollen in the main mass of liquids overnight it will speedily go into solution on the addition of the ethyl acetate if the agitation is good. For making small quantities of these solutions by hand it is advisable to use a receptacle wide at the bottom.

CHAPTER XV.

SYNTHETIC RESIN ADHESIVES.

THE manufacture of adhesive solutions based on synthetic resins presents many points of similarity to their manufacture from cellulose nitrate as discussed in the preceding chapter. The operation is much simpler, though, and enables the production of very good, strong and water-insoluble adhesives with higher percentages of dry material.

The *vinyl resins* are the products that have, so far, been of main interest to the adhesives maker. These materials are made from acetylene and acetic acid, which react in the presence of a catalyst to give a vinyl ester. The primary ester is in some cases polymerised by heating in the presence of a sodium peroxide catalyst. These vinyl synthetic resins, sometimes co-polymerised with acrylic or other resinoids, are used largely as adhesives in the production of laminated safety glass. Their employment for ordinary adhesives purposes is, however, developing rapidly. In Germany, they are manufactured by the I. G. Farbenindustrie A.-G. under the trade name "Mowilith." They are made in Canada by Shawinigan Chemicals, Ltd., under the trade names "Gelvars," "Formvars," "Alvars," "Butevars," etc., whilst they are also manufactured in the United States. At present they are not made in the United Kingdom, but if the projected manufacture of carbide by hydro-electrical power in the Highlands of Scotland materialises, the cheap and plentiful acetylene then available may be followed by the manufacture of these acetylene-derived synthetic resins. The writer's experience, however, has so far been wholly with the "Mowilith" resins.

Four types are made, differing in the viscosities of their solutions, namely :—

"Mowilith NN,"	Low viscosity.
"Mowilith N,"	Low viscosity.
"Mowilith H,"	Low viscosity.
"Mowilith HH,"	High viscosity.

These resins retain their solvents for quite long periods and after complete drying leave a colourless film which is flexible, hard and

strong and which improves with the lapse of time. The main drawback is high price.

The resistance of the dried films to water is not quite so good as that of the films from cellulose solutions, but this disadvantage can be overcome by the use of solvents such as benzene, toluene and butyl acetate, which are not miscible with water, and by the addition of a good non-hygroscopic plasticiser such as tricresyl phosphate. The addition of tricresyl phosphate in the proportion of about 15 per cent. of the weight of the dry resin further improves the adherence of the film to smooth surfaces such as sheet iron, glass, etc.

Grades " N " and " H " of the resin are the ones generally used, as they give an adhesive solution of the concentration and density most frequently required. The best and most economic solvent for " Mowilith " resin is benzene.

Formula G-1.

Synthetic Resin Adhesive Solution.

Benzene, solvent grade,	300	Allow to dissolve and stir from time to time.
" Mowilith H,"	100	

The addition of coumarone resin or of ester gum enables a reduction in the cost of the solution and also increases its stickiness and density, with the production of a thicker dried film.

Formula G-2.

Synthetic Resin Adhesive Solution.

Benzene, solvent grade,	300	Allow to dissolve and stir from time to time.
Ester gum,	30	
" Mowilith H,"	100	

In this type of adhesive solution use can also be made very advantageously of the azeotropic mixture of alcohol and benzene discussed in the chapter on Cellulose Adhesives. This mixture is very useful when the adhesive solution is to be employed on metallic surfaces, since the oxidising power of the solution is then less pronounced. Further, the benzene-alcohol mixture is superior to benzene alone on the grounds of actual solvent power and of odour. If two tinplate boxes are taken and one filled with a solution of " Mowilith " in benzene and the other with a solution of " Mowilith " in benzene-alcohol and the bottoms of these boxes are scratched, oxidation will be noted around the scratch in the former case but not in the latter.

An improved product of this type is given in Formula G-3, which also contains a little butyl alcohol, added to prevent blush troubles in warm or damp weather.

FORMULA G-3.

SYNTHETIC RESIN ADHESIVE SOLUTION.

Benzene, solvent grade,	204	Allow to dissolve and stir from time to time.
Denatured alcohol, 95 per cent.,	96	
Butyl alcohol,	20	
Ester gum,	30	
"Mowilith H,"	100	

For cases where it is desired to mitigate the somewhat penetrating odour of the composition given in Formulæ G-1, G-2 and G-3, the esters can be utilised as solvents. A typical solution will then be :—

FORMULA G-4.

SYNTHETIC RESIN ADHESIVE SOLUTION.

Ethyl acetate,	300	Allow to dissolve and stir from time to time.
Coumarone,	30	
"Mowilith H,"	100	

Within recent years the manufacture of transparent cellulose wrapping materials, of a type of which the product "Cellophane" is a well-known example, has grown into an industry of very considerable importance, these materials being used widely for the wrapping, by automatic means, of many packeted products, such as cigarettes and foodstuffs. The choice of a suitable adhesive for the purpose is not a simple one. The adhesives based upon solutions of synthetic resins have proved suitable, providing care be taken to utilise solvents which, whilst possessing a certain solvent action on the cellulose film, are without penetrating odour. The ethers of ethylene glycol have been found very serviceable for the purpose, and in particular the monomethyl ether of ethylene glycol, which is manufactured in Germany by the I. G. Farbenindustrie A.-G., and in the United States by the Carbide and Carbon Chemicals Corporation of New York under the trade name of "Methyl-Cellosolve." The monomethyl ether is, however, somewhat hygroscopic. It is advisable to add to it a little butyl alcohol, or better still, a little of the monobutyl ether of ethylene glycol, to prevent clouding during the drying of the adhesive. The addition of a plasticiser such as tricresyl phosphate to the solution is further recommended, both to increase the adhesion and to render the joint made rather more flexible.

FORMULA G-5.

ADHESIVE FOR IMPERMEABLE TRANSPARENT CELLULOSE WRAPPING.

Ethylene glycol monomethyl ether,	1,600	Allow to dissolve and stir from time to time.
Ethylene glycol monobutyl ether,	16	
Tricresyl phosphate,	15	
"Mowilith H,"	100	

The *phenol-formaldehyde synthetic resins* find quite a substantial application as adhesives in the manufacture of wood veneers, but their application is by the hot method and so does not really come within the scope of this book. These synthetic resins also find a certain use, dispersed in aqueous or non-aqueous media, as binders for brush-setting cements, sand-core binders for foundry castings, etc.

The most recent development in the application of synthetic resins as adhesives follows the discovery in the United States that distinctive properties are conferred upon synthetic resins of the *urea-formaldehyde type* when the condensation between the urea and the formaldehyde is effected in the presence of zinc chloride. New resins made by this process, and in which the zinc chloride appears to be combined as part of the molecule, have been introduced under the trade name "Lauxite" and are reported as having already occasioned wide interest in the plywood industry.

CHAPTER XVI.

RUBBER AND LATEX ADHESIVES.

THE occurrence and nature of latex and the production of coagulated rubber were discussed in the chapter on Raw Materials. By the employment of either of these materials it is possible to obtain adhesives of unique properties and which find their principal utilisation in connection with leather and rubber. In the boot and shoe industry large quantities of latex are used as a cement for sticking (*a*) leather to leather, (*b*) leather to crêpe sole or vulcanised rubber, (*c*) canvas, (*d*) felt.

Dealing first with dry rubber itself, the two principal methods of making adhesive solutions are as follows:—(1) Employing non-vulcanising solutions of rubber, and (2) employing solutions of rubber which are subsequently vulcanised.

The most suitable grade of raw rubber for making adhesive solutions is *pale crêpe*, the quality sold under the name of "smoked sheet" being somewhat more difficult to dissolve.

Rubber is soluble in aromatic hydrocarbons (benzene, toluene, xylene, solvent naphtha, etc.), aliphatic hydrocarbons (petrol, petroleum ether and benzine), chlorinated hydrocarbons (carbon tetrachloride, chloroform, methylene chloride, dichlorethylene, trichlorethylene, etc.), as well as in a range of miscellaneous solvents including carbon bisulphide, the naphthenic acids, the glycol derivatives, etc.

In practice, benzene is the *solvent* usually employed owing to its price and to its universal availability. It is a true solvent for rubber. Its boiling point, 80° C., is sufficiently high to avoid clouding of the film by too rapid evaporation, there being no danger of the precipitation of atmospheric moisture on a film of the adhesive which is drying-out.

Petrol is undoubtedly cheaper than benzene, but its solvent power is inferior, whilst it has a distinctly retarding influence on the vulcanisation process.

Trichlorethylene is an excellent rubber solvent and has the

additional advantage of non-inflammability. Its price and its rather high specific gravity are against it, however, for many uses.

Carbon tetrachloride can be added to diminish the inflammability of the benzene, but dichlorethylene is probably the better additive for this purpose, since it is less toxic, facilitates the vulcanisation process to the greatest extent and decreases to the most pronounced degree the viscosity of rubber solutions. Its drawback is its low boiling-point, with a tendency to produce a cloudy film. A mixture of one-third dichlorethylene and two-thirds benzene is only slightly inflammable and the flame is easily extinguished.

Unless exceptional precautions are taken, carbon bisulphide is a very dangerous solvent to use owing to its low boiling-point and exceptionally ready inflammability.

The rubber solution is made simply by placing the rubber in contact with the benzene. The rubber particles at first swell, but later a homogeneous solution is obtained. Using this simple contact method, however, production of concentrated rubber solutions is difficult owing to the swelling phenomenon referred to.

Speed of solution can be accelerated by a number of methods, the most important of which is the intervention of the mechanical factor. The dried rubber preserves to a large extent the structure of the rubber particles in the latex. These particles are composed of an outer skin of high viscosity, which is difficultly soluble in benzene, and an inner mass of lower viscosity which is very soluble in benzene. By prolonged mixing and mastication the outer skin is destroyed, the internal contents of the globules entering into solution and diminishing the viscosity. It is also probable that under the influence of intense mastication in the presence of a solvent, the viscous external phase also enters more or less into perfect solution.

The viscosity of these rubber solutions can be reduced by other methods: (1) By the addition of such materials as eucalyptus oil or turpentine oil; (2) by the addition of very small quantities of organic bases or acids, for instance, one part of piperidine to 20,000 parts of the solution, stearic acid, rosin or benzene-soluble vulcanisation accelerators; (3) by the intervention of heat.

In practice, the best results are obtained by the adoption of an enclosed mixer or, better still, masticator capable of working the rubber into the form of thick paste in the presence of a small quantity of benzene. The remainder of the benzene, together with the dichlorethylene to reduce the viscosity and inflammability, is added later. Working under these conditions, solutions with an average ratio of one part of crêpe rubber to ten parts of solvent, and which spread easily, can be obtained. Under less favourable conditions

it may be necessary to double or treble this proportion of solvent; for instance, when working with trichlorethylene or with viscous rubbers.

FORMULA H-1.

SIMPLE RUBBER SOLUTION.

Crêpe rubber, . . .	100	Dissolve.
Benzene, solvent grade, .	1,500	

FORMULA H-2.

IMPROVED RUBBER SOLUTION.

Crêpe rubber, . . .	100	Dissolve.
Dichlorethylene, . . .	300	
Benzene, solvent grade, .	700	

The cost of these solutions can be reduced and their properties as adhesives enhanced by the addition of suitable inorganic *filling materials*, among which carbon black, " Thermatomic black " (a special grade of carbon black), magnesium carbonate, colloidal clays, zinc oxide, lithopone, kieselguhr, kaolin, barium sulphate and calcium carbonate may be mentioned. These products increase the density of the solution and consequently the final thickness and strength of the rubber layer left after evaporation of the solvent. Other things being equal, the value of these filling or reinforcing agents depends largely upon the fineness of their state of sub-division. Probably the two best materials are " Thermatomic black " and ordinary carbon black. Zinc oxide occupies a somewhat intermediate position, but in solutions which are subsequently to be vulcanised its presence is practically indispensable. Calcium carbonate is of main value where cost considerations are almost the sole concern. " Thermatomic black " is a carbon black made by the thermal decomposition of natural gas in the absence of oxygen. It incorporates readily with rubber or rubber solutions and unlike ordinary carbon black, does not retard the speed of vulcanisation, but actually accelerates it slightly.

Carbon black is, however, the reinforcing material most frequently employed. This is a gas-black obtained by the incomplete combustion of natural gas, the carbon being precipitated on suitable cold surfaces.

The percentage of loading material to be employed depends upon the density desired in the finished solution, but in the case of carbon blacks 40 per cent. on the weight of the rubber may be taken as an average figure. Equal weights of black and crêpe rubber are about the highest that can be used.

With rubber solutions for use as adhesives, the natural and synthetic resins are also practicable loading materials, coumarone

resins and ester gums being the best in this connection. Up to 50 per cent. of these resins on the weight of the crêpe can be added without any marked diminution in the softness and elasticity of the dried rubber film. The presence of these resins, as a matter of fact, increases the water-resistance of the film. In practice, the addition of 10 to 20 per cent. of ester gum on the weight of the crêpe is probably best.

FORMULA H-3.

RUBBER-RESIN ADHESIVE SOLUTION.

Crêpe rubber,	100	Dissolve.
Ester gum,	10	
Dichlorethylene,	300	
Benzene, solvent grade,	700	

The use of natural rosin in this connection is not advised. Its acids alter the viscosity of the solution and give a film which is too sticky. Rosin should be added to rubber adhesives only for such purposes as fly-papers, etc.

There are two general methods for the *vulcanisation* of rubber, the cold process in which the vulcanising agent is a solution of sulphur chloride in a solvent such as carbon bisulphide, and the hot process in which the vulcanising agent is sulphur. In practice, the action of the sulphur is always speeded up by the addition of an " accelerating agent." Until about twenty-five years ago the metal oxides, litharge in particular, were the sole products used for this purpose, but to-day numerous organic compounds which are far more efficient vulcanisation accelerators are available. These are usually employed in the presence of zinc oxide, which functions as an activating material.

The use of organic accelerators is not confined solely to the hot process, equally satisfactory results being obtained in the cold method. In general, these accelerators reduce the time required for the vulcanisation process, diminish the amount of sulphur necessary to attain any definite degree of vulcanisation and, by reducing the quantity of free sulphur in the vulcanised material, practically obviate the possibility of free sulphur efflorescing to the surface—" blooming "—of the vulcanised material after a more or less prolonged period of storage.

The organic accelerators most frequently employed are piperidine piperidyl dithiocarbamate, diphenylguanidine, triphenylguanidine, thiocarbanilide, mercaptobenzothiazole, aldehyde-ammonia, para-nitrosodimethylaniline, and hexamethylenetetramine, although it is probable that something like 200 of such organic accelerators are at present used in the rubber industry.

The organic accelerators are usually classified, according to their

speed of reaction, into ultra-accelerators (an example being materials of the dithiocarbamate type), rapid accelerators (*e.g.*, diphenylguanidine), moderate accelerators (*e.g.*, aldehyde-ammonia), slow accelerators (*e.g.*, thiocarbanilide).

In the production of *self-vulcanising rubber solutions* for use as adhesives there are several conditions to be observed. Vulcanisation should be neither too slow nor too rapid, and should not proceed beyond a definite degree. In a self-vulcanising rubber solution containing a soluble accelerator and a sufficient quantity of sulphur, the vulcanisation process proceeds at ordinary temperatures over several days until, in fact, the whole of the free sulphur has gone into combination. In this case there is the risk of over-vulcanisation. If, however, the percentage of sulphur in the solution is reduced to the bare minimum necessary, vulcanisation takes place too slowly for adhesive purposes. This latter trouble cannot be corrected by increasing the quantity of accelerator used, for not only are these latter materials usually rather costly, but when employed above a certain maximum amount the additional quantities used have very little influence on the speed of vulcanisation. This will be understood from the fact that only that quantity of accelerator which is soluble in the rubber at the temperatures employed functions in speeding up the reaction.

There is another kind of unwanted behaviour which rubber solutions when used as adhesives may show. If a normal self-vulcanising solution be spread over a sheet of glass, after the evaporation of the solvent and the expiry of two to three days, a perfectly vulcanised rubber film is obtained; yet this same solution applied to rubber surfaces may show no signs of vulcanisation even for six or eight days. The reason is that the sulphur, or the soluble accelerator in the solution, has migrated to the rubber mixture to which the solution has been applied.

From the viewpoint of the adhesives maker, therefore, it is inadvisable to reduce the quantity of sulphur in these self-vulcanising solutions to the lowest possible figure since, under such conditions, the sulphur, being wholly soluble in the rubber, tends to migrate from the solution into the rubber surface on which it is employed. If, on the other hand, a slight excess of sulphur over the theoretical is employed, the adhesive solution and the rubber surface to which it is applied will tend to reach a state of equilibrium in respect to their sulphur contents, an adequate amount of sulphur for the actual vulcanisation still remaining in the solution.

In practice, the quantity of sulphur aimed at in an adhesive solution is such that will give a satisfactory result in from two to three days at ordinary temperatures. The best method of preventing

the migration of the accelerator is to use a non-soluble accelerator or one which does not migrate, such as the zinc salt of an ultra-accelerator.

Whatever the composition of the adhesive solution, however, it it is always advisable to use a slight degree of heat to activate the vulcanisation process before migration phenomena have taken place to any extent. Actually, a temperature of 40° to 70° C. is the most suitable.

As has been pointed out, the organic vulcanisation accelerators function most effectively in the presence of zinc oxide. By itself, this oxide is only a very weak accelerator, but it activates the organic accelerators and has the further advantage of being an excellent reinforcing loading material for the vulcanised product. This activation can be amplified by increasing the fineness of distribution of the zinc oxide in the solution by the supplementary addition of fatty acids such as oleic acid or stearic acid, it being probable that zinc salts of these acids are produced. The use of these fatty acids is additionally interesting as it results in a diminution of the viscosity of the rubber solution.

The two surfaces to be joined may be treated with one of the three simple solutions, H-1, H-2 or H-3. One of the surfaces is then treated with a 2 per cent. solution of sulphur chloride in a solvent such as benzene and the joint made under slight pressure.

In preparing adhesive solutions in which sulphur and an accelerator are employed, the crêpe rubber, sulphur, zinc oxide and stearic acid may be dissolved in, or mixed with, the benzene, and the accelerator (in conjunction with benzene) added only at the moment the solution is to be used. This method of working has the inevitable disadvantage that the actual solution can only be made up just when it is to be used and any which is not used is wasted.

A more rational procedure is to employ two solutions, one containing the sulphur and the other the accelerator. This really is the most practicable method of working, for whilst the two solutions remain separated they can be kept indefinitely. As soon as they are mixed, vulcanisation commences slowly, even at ordinary temperatures. The two solutions suggested are as follows :—

FORMULA H-4.

SELF-VULCANISING ADHESIVE RUBBER SOLUTIONS.

Sulphur,	6	Zinc oxide,	10
Stearic acid,	1	Zinc salt of ultra-accelerator,	2
Benzene,	700	Benzene,	700
Dichlorethylene,	300	Dichlorethylene,	300
Crêpe rubber,	100	Crêpe rubber,	100
	A		B

The dichlorethylene can be omitted and replaced by an equivalent weight of benzene, whilst loading materials in amounts from 40 to 100 per cent. of the weight of the crêpe can be added. For use, the two solutions are mixed in equal volumes. Since the first solution is transparent and the second an opaque white, there is little danger of the two being confused by workmen. The mixed solution commences to set after about two days, according to the temperature and the solvent used.

For the reasons discussed above, it is preferable to use, if possible, a higher temperature. For instance, vulcanisation is complete in about two minutes at 140° C., in three or four minutes at 115° C. and in one to two hours at 80° C. At ordinary temperatures, vulcanisation requires, as a rule, two to three days.

To prevent gelatinisation, these solutions should be kept out of contact with direct sunlight and should preferably be stored in opaque receptacles.

Since *natural latex* is composed of globules of rubber dispersed in an aqueous serum, it is easily understandable that such a solution has poor adhesive power. Further, the production from latex of self-vulcanising solutions by the methods outlined above for crêpe rubber is not feasible for the following reasons.

The addition to latex of dry powder causes coagulation, due partly to the absorption of the liquid by the dry powder and partly to the electrical effect of the positive charge carried by materials such as carbon black and metallic oxides.

The second difficulty is due to the lack of solubility, and consequent lack of contact with the latex, of the various additives. To avoid these drawbacks when working with latex, the following methods are used.

The sulphur is added in a soluble condition in the form of sodium sulphide or, better still, as ammonium sulphide or as colloidal sulphur in aqueous suspension. The insoluble constituents are added only after prolonged agitation with an aqueous solution containing an emulsifying agent and an electronegative colloid (gelatin, gum arabic, etc.), or, much more simple and preferable, by using the prepared colloidal solutions (obtained in a colloid mill) which are now articles of commerce.

The types of adhesive solutions made from latex may be classified as follows:—(1) Non-vulcanising latex emulsions: (*a*) Addition of a water-miscible adhesive. (*b*) Addition of a water-immiscible adhesive. (*c*) Addition of a solvent. (*d*) Addition of a solvent and a water-immiscible adhesive. (2) Vulcanising latex emulsions: (*a*) Vulcanisation by ammonium sulphide. (*b*) Vulcanisation by the addition of an accelerator. (*c*) Vulcanisation by the mixture of two solutions.

Quite a number of water-miscible adhesive substances are suitable for incorporation with latex. In practice, selection is influenced by the desirability of avoiding the use in this connection of water-miscible adhesives with the following properties :—Those whose gelatinising properties may mean an undue increase in the viscosity of the latex ; those which are too liable to bacterial decomposition ; those which are too alkaline, too acid or hygroscopic ; and those which are too costly.

The water-miscible adhesive that might be considered the ideal one for admixture with *non-vulcanising latex adhesives* is the strong modified starch adhesive given on page 112 under Formula C-3. A mixed-base adhesive solution of this type will give a film which is colourless, flexible yet strong, neutral, waterproof, stable to putrefactive influences and, above all, extremely cheap, a combination of properties that cannot be found to the same degree in any other adhesive.

Formula H-5.

Strong Latex-Starch Adhesive.

Latex, 40 per cent., ...	100	Mix.
Strong starch adhesive, Formula C-3, . .	200	

The results obtained by the use of this strong modified starch adhesive in combination with latex are remarkable. By mixing a 40 per cent. latex with twice its weight of the strong modified starch adhesive referred to, there is obtained, on drying, a film which is practically identical in flexibility and elasticity with that produced by the latex alone. The cost of the Formula C-3 starch adhesive is very low and the economic advantages of its employment by the industries making use of rubber latex for its adhesives properties, are marked.

For certain industrial uses in connection with latex, it may be desirable to employ this strong starch adhesive in an absolutely neutral state. In such cases final neutralising is effected with dilute phosphoric acid. Hydrochloric acid should not be used for this purpose (as in Formula C-1) for if only very small quantities of free hydrochloric acid are present, there will be marked danger of coagulation of the latex. The salts of phosphoric acid, on the other hand, function as distinct stabilising and preserving agents for latex.

In regard to the introduction of water-immiscible adhesives into latex, it is inadvisable, for reasons previously given, to use ordinary rosin (though it can be used as sodium resinate emulsion) ; ester gum is preferable. Before addition to the latex, the ester gum should be

emulsified in the presence of sodium resinate, an emulsified rosin oil, ammonia or triethanolamine, etc.

The processes just mentioned are covered in numerous patents and are mentioned here mainly for record. In practice, according to the writer's experience, far better results are given by the processes which are now to be described.

All the usual processes for the improvement of latex for use as an adhesive have this in common: First, where rosin is used, it is added in the form of an emulsion obtained either by partial saponification or by emulsification with suitable products. The drawback in this case is that the adhesive properties of the latex are increased only to a comparatively slight extent, since the actual amount of rosin added as such is very small. The substitution of soda by ammonia or its organic derivatives when making emulsions for addition to latex has been suggested, but the methods do not seem to hold out any marked advantage over the ordinary soda saponification method. Secondly, if the addition of rosin is to be carried to a point at which a marked improvement is effected in the adhesive properties of the latex, the quantity of rosin and consequently emulsifying agents added, becomes very high. The emulsifying agents remain, to a large extent, in the dried film and detract from its properties of flexibility, elasticity, etc. Thirdly, in such a system, where the rubber forms the disperse phase and the emulsion the continuous phase, the water-resistance of the rubber is considerably reduced. The following methods are advanced as much more rational (Roger Dulac Processes).

By the addition of a suitable solvent to ordinary latex, with the object of liberating the full adhesive value of the rubber itself, all the advantages aimed at by the use of water-miscible resin derivatives are secured without their corresponding disadvantages. This result is obtained by the addition to the latex of a cheap solvent, the boiling-point of which should be a little higher than that of water, with the object of ensuring that at the end of the evaporation of the mixture of water and solvent the latter only will be present, if only in small quantities, and will act on the dried rubber film in a manner similar to the usual action of a solvent on ordinary crêpe or sheet rubber.

Toluene is advanced as the best solvent for this purpose. Its boiling-point (commercial grade) is 109° to 110° C. As the quantity employed is small and as, during most of the drying period, water is also present, fire risks are negligible and there is consequently no need to consider the substitution of the toluene by a non-inflammable solvent.

The dispersion of the toluene and the latex is secured by the preliminary addition to the latter of a small quantity of an emulsifying agent. Sulphonated oils, and particularly neutral ammonium

sulphoricinoleate, have proved most suitable. After the addition of the toluene, the emulsion obtained is very milky and adhesive, similar in physical consistency to a very fluid cream, and spreads well. The initial simple dispersion of rubber globules in an aqueous serum, as existing in the latex, has been converted into an aqueous emulsion of rubber solution.

The quality of the solution depends to some extent upon the relative and actual quantities of toluene and emulsifying agent used. If insufficient toluene be added, the adhesive power of the latex mixture is not increased to its fullest extent. If the quantity of emulsifying agent is not high enough in relation to the quantity of toluene introduced, the latex will coagulate. The higher the percentage of toluene employed, the more creamy does the latex become. There is no danger in using too much sulphoricinoleate, the only effect of additional quantities over the necessary minimum being to increase the degree of dispersion of the emulsion.

The three mixtures given in the following formulæ have proved very successful as latex adhesives, with properties considerably better than the untreated latex.

Formula H-6.

Latex Adhesive Improved by the Addition of a Solvent.

	I.	II.	III.	
Latex, 40 per cent.,	100	100	100	Mix carefully.
Neutral ammonium sulphoricinoleate,	0·350	1	3	
Toluene,	30	100	200	—Emulsify.

A further improvement in the latex type of adhesive lies in the use of a resin in addition to the solvent. Similar advantages are obtained as in the case of the incorporation of a resin with a cellulose solution, as discussed in Chapter XIV. The hardness, strength, impermeability and adhesive power of the dried film are all increased provided, as in the case now under consideration, the resin is introduced as such and not in the saponified or emulsified condition.

The employment of an additional emulsifying agent is not necessary in a modified adhesive solution of the H-6 type, since both the ammonium sulphoricinoleate and the dispersed solvent combine to hold the added resin in perfect suspension. The film obtained on drying is quite as homogeneous as one obtained on drying the untreated latex.

Theoretically there is no limit, within reason, to the amount of resin that can be added to an adhesive material of this type, but in

practice it is not desirable to use more resin than 10 to 20 per cent. of the weight of the dry rubber. Rosin itself is ruled out here by its high acidity. Ester gum can be used, but the best results are obtained by the employment of a cheap neutral resin such as coumarone.

FORMULA H-7.

IMPROVED LATEX ADHESIVE.

Latex, 40 per cent.,	100	Mix carefully.
Neutral ammonium sulphoricinoleate,	0·350	
Toluene,	30	Emulsify.
Coumarone,	8	

Bentonite, or colloidal clay, is another material which can find a very advantageous field of application in latex adhesives. The incorporation of bentonite in latex is difficult. It cannot be added in the dry state, and even if first mixed well with 10 to 20 times its weight of water, the attainment of a homogeneous mixture with latex is a troublesome operation. A way out of the difficulty is found in the following method, which is equally applicable to the incorporation of other intractable material with latex. The bentonite is mixed with an emulsifying agent, in which it does not swell, until a smooth paste is obtained. Such a paste will rapidly go into homogeneous dispersion when mixed with an aqueous medium either containing or not containing an adhesive.

In the present case, the bentonite is mixed with an equal weight, or possibly rather more than its own weight, of neutral ammonium sulphoricinoleate. The emulsifying agent fulfils three functions: It reduces the surface tension of the aqueous serum of the latex; it acts as a protective colloid for the particles of bentonite, and it facilitates the impregnation of the bentonite by the aqueous medium. The bentonite-emulsifying agent mixture mixes with the latex with remarkable ease and rapidity. When working with small quantities, all that is necessary is to spread the paste thinly round the inside walls of the receptacle in which the adhesive is being made. The latex is then added and, on giving the mass a slight stirring, a uniform product is obtained almost at once. The toluene is then added and stirring continued a little longer. Working on the larger scale and in mixing plant, the production process is still easier.

The addition of bentonite not only improves the adhesive power of a latex, but also enhances stability. With latices more concentrated than 40 per cent. the process is probably of even more interest as it enables reduction in the amounts of emulsifying agent and toluene necessary.

Vulcanising Latex Emulsions.—Vulcanisation with ammonium sulphide: The two surfaces to be joined are coated with one of the emulsions H-5, H-6 or H-7. One of the surfaces is then treated with a dilute solution of soluble sulphur in the form of yellow ammonium sulphide (ammonium polysulphide).

Vulcanisation by the addition of an accelerator: A solution is made up on the basis indicated in the formula below, containing all the constituents shown, with the exception of the accelerator. This last-mentioned is added immediately prior to use, diluted in a solution containing a wetting agent.

Vulcanisation by the mixture of two solutions: This is the most rational of the three methods. The principles involved are the same as in the case of the vulcanisation of rubber solutions in organic solvents. The employment of stearic acid or of accelerators with an acid reaction is to be avoided if the possibility of the coagulation of the latex is to be ruled out. In any event, since the ingredients of the dispersions are already in a sufficiently fine state of subdivision, there is no point here in the use of stearic acid. Another consequence of the high degree of dispersion of the reactants is that the quantity of colloidal sulphur and colloidal zinc oxide can be kept low. In regard to the former, from 1 to 1·5 per cent. on the weight of the dry rubber is adequate, and in regard to the latter from 2 to 3 per cent.

Formula H-8.

Self-vulcanising Latex Emulsion.

Latex, 40 per cent.,	100	A	Latex, 40 per cent.,	100	B
50 per cent. sulphur emulsion,	1·6		30 per cent. zinc oxide emulsion,	5·5	
			Ultra zinc accelerator,	0·8	

The accelerator is best first mixed with the zinc oxide emulsion before adding to the latex to produce solution B.

Instead of using ordinary latex, one of the latex emulsions of increased adhesive power, as described above, can of course be used.[1]

Since natural latex is essentially a dispersion of rubber globules in an aqueous medium, the possibility of reversing the coagulation process, that is, of converting ordinary dried rubber into the latex condition—in a manner similar to that in which a sheet of dry gelatin

[1] The reader interested in latex for its adhesive or other uses may be referred to the highly useful handbook "Rubber Latex" (4th Edition) that has been compiled for the Rubber Growers' Association Inc., by H. P. Stevens, M.A., Ph.D., F.I.C., and W. H. Stevens, F.I.C., and which is obtainable, *gratis*, from the Association at 19 Fenchurch Street, London, E.C. 4.

swells and finally dissolves in water—exists. This reversion has in fact been effected by a number of workers.

Liquid latex is undoubtedly one of the products of the future. Its applications are growing for a number of reasons, of which the following are the principal: Avoidance of the use of costly and inflammable solvents; the possibility of working with solutions of high concentrations—up to 75 per cent., a figure which cannot possibly be reached with solutions of rubber in organic solvents; the rubber in latex has its full strength and "nerve," since the operations of solution or mastication have an unavoidably adverse effect on these properties.

The drawback to the use of natural latex is, of course, the fact that freight has to be paid on its water content as well as on its rubber content during its carriage from the producing country to the consuming point, whilst container costs are higher than with dried rubber. The logical solution of the problem would seem to reside in the transport of dried rubber and in its reconversion into a highly concentrated artificial latex at the place where it is to be used.

The manufacture of *artificial latex* involves the same principles as those underlying the production of all aqueous emulsions. The intermicellar attraction between the rubber globules in the coagulated rubber can be diminished either by a modified treatment with a solvent or by mechanical stretching of the dried rubber accompanied by a rise in temperature. To the plastic or pasty mass obtained by either of the above methods there is added an emulsifying agent (saponines, oleates, etc.) or a hydrophylic protective colloid such as gelatin, casein, gum arabic, resinates, etc., or a mixture of the above types of materials. The emulsifying agent may be produced directly in the mass by first adding a resin, oil or fatty acid and then an alkali, preferably ammonia, in quantity sufficient to neutralise the fatty acid or resin or to saponify the fatty oil.

It should be noted that in such a system, where the rubber forms the disperse phase and the aqueous serum (including the emulsifying agent and/or the protective colloid) forms the continuous phase, the impermeability of the rubber is reduced. Consequently, as in the case of emulsions made from natural latex, it is advisable that the quantity of dispersing agents employed be as low as possible and that materials of pronounced hygroscopicity be avoided altogether.

In the first of the processes for making artificial latex noted above, the rubber is treated in a masticating machine with three times its weight of benzene. A concentrated solution of saponine is then added slowly. After prolonged mixing the emulsion first formed, in which the rubber solution is the continuous phase, reverses, the solution of saponine becoming the continuous phase and the rubbe the disperse

phase. When this point is reached the emulsion is diluted with water, the agitation being continued. The benzene is recovered by distillation.

To avoid the employment of a costly and inflammable solvent, and the necessity for the adoption of a solvent recovery process, the second of the methods for the production of artificial latex noted above has advantages. In this method the rubber sheet is worked on the mixing rolls until it is hot and plastic. To the rubber is then added one-twentieth of its weight of ordinary glue that has been swollen in water and the working on the rolls continued until the glue has been thoroughly incorporated in the rubber. The mass is then transferred to a two-blade mixer and water added in amount sufficient to produce an emulsion with a total water content of 10 per cent. inclusive of the water that was introduced with the glue. The next step is to add a hot concentrated solution of saponine in water (one part saponine to two parts water), the quantity of this last-mentioned solution being one-seventh of the weight of the rubber in the mass being treated. The emulsion is then treated with hot water until the consistency of the milky emulsion produced is similar to that of the natural latex it is desired to reproduce.

This last mentioned process may also be operated in the reverse direction. The hydrophylic protective colloid can be worked into a thick mass on the rubber mill and then treated with small quantities of rubber that has been softened by mastication on the rolls in the presence of sodium carbonate, borax, ammonia or other peptising agent.

When using synthetic latices for the manufacture of adhesive products, the methods are similar to those with natural latex, though regard should be paid of course to the nature and amount of the emulsifying and wetting agents present.

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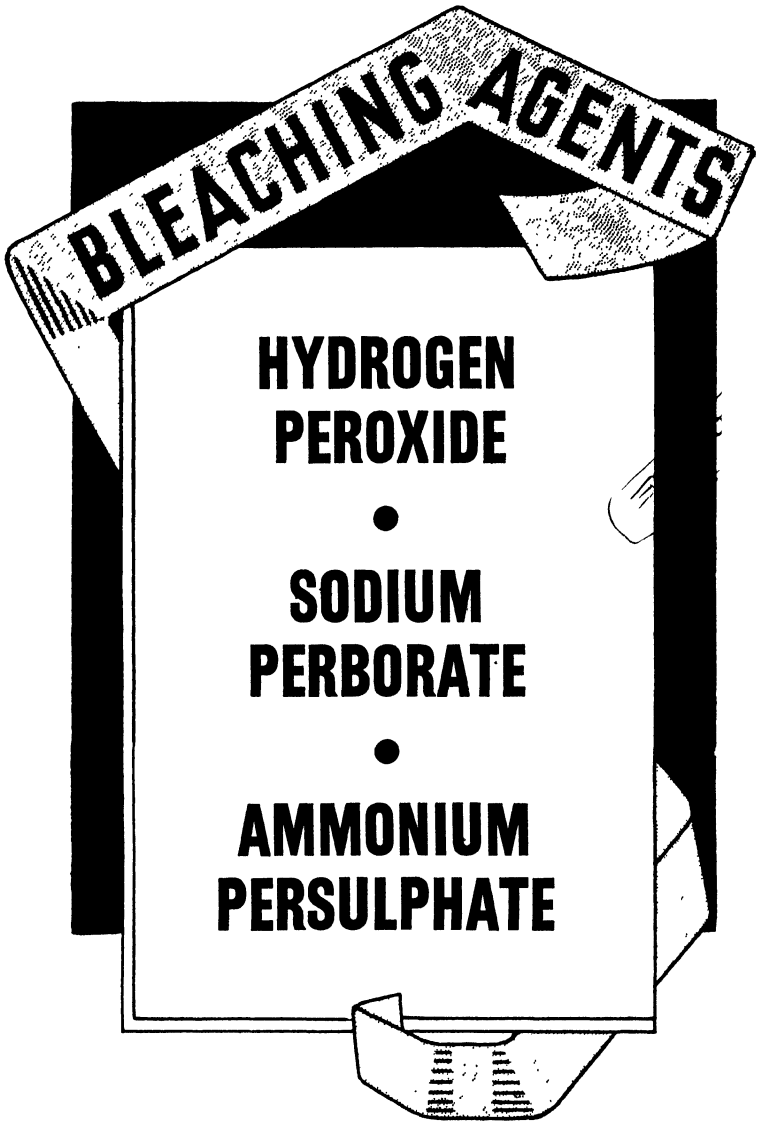

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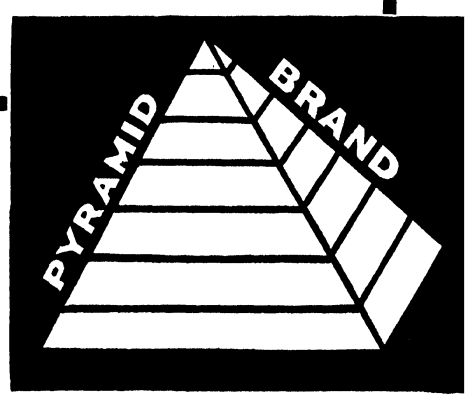

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